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BORON IN IRON AND STEEL

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R. S. DEAN AND B. SILKES

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BORON IN IRON AND STEEL[1]/

By R. S. Dean[2]/ and B. Silkes[3]/

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INTRODUCTION

General Review

Boron compounds have been considered for many years as possible additions to iron and steel. A very recent use of boron-steel rods was for the control of neutron intensity in the graphite-uranium pile at the Clinton plutonium plant.(130).4/

Norris(129) reports that slags containing boric oxide reduce the ferrous oxide content of steels and thereby the aluminum required for deoxidation. Boron is not considered an alloying element, but minute amounts produce what is often called a "needled" steel. The study of a series of iron-boron alloys by convenient steps, starting with iron containing no boron, indicated that boron was a hardening agent and made the iron very difficult if not impossible to forge. Then came the discovery that very minute traces of boron are quite different from the smallest amount previously thought worthy of study.

The use of substantial quantities of boron improves the properties of cast iron and steel. Guillet(37) reports that the tensile strength and elastic limit of steel increase with the quantity of boron introduced and that the percentage of elongation diminishes. After hardening at 850° the strength and elastic limit are very much increased. Walter(168), in his patent issued in 1924, claimed that 0.001 to 0.100 percent of boron is incorporated in ferrous metals such as steel or cast iron to improve the texture of the metal or to render it self-hardening.

In 1937 Naton and Piwowarsky(70) observed that increasing the boron content of cast steel, containing 0 to 5 percent nickel, from 0.02 to 0.1 percent, resulted in all instances in an increase of strength and hardness both in the normally annealed and in the quenched and tempered state. Tempering at 50°, 150°, and 250° reduced the hardness in all boron-free steels, while the boron-containing specimens retained their hardness or showed a slight precipitation hardening. All boron specimens showed a

4/ Numbers in parentheses refer to items in the bibliography at the end of this paper.

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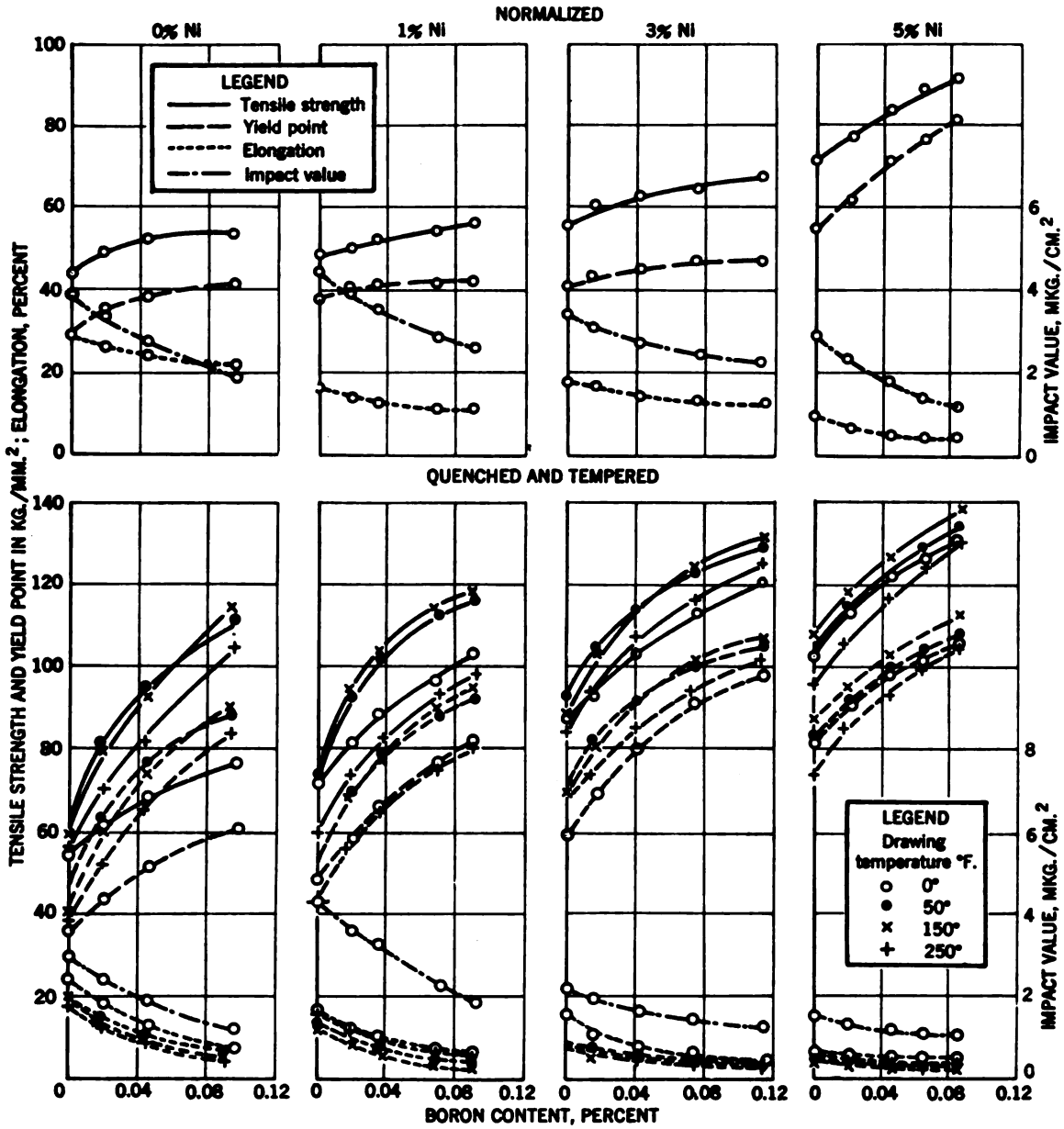

FIGURE 1.- Effect of boron on mechanical properties of Bessemer cast steel with 0.13 percent carbon and 0 to 5 percent nickel after varied heat treatment.

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finer grain. Tempering made the martensite of the boron-containing steels considerably finer, while in the boron-free steels it began to disintegrate. Figure 1 shows the effect of boron on the mechanical properties of a Bessemer cast steel with 0.13 percent C and 0 to 5 percent Ni.

Hirsch(72) describes a nickel-boron cast iron containing carbon 2.50 to 3.25 percent, boron 0.70 to 1.10 percent, silicon 0.50 to 1.50 percent, manganese 0.50 to 1.25 percent, nickel 3.50 to 4.50 percent, phosphorus 0.05 percent maximum, and sulfur 0.05 percent maximum, which has a melting point of 1975° F. and extreme resistance to abrasion. This permits surfacing of steel or cast iron by molten-metal contact and subsequent diffusion.

Yensen(44) studied the effect of boron upon the magnetic and other properties of electrolytic iron melted in vacuo. His results are summarized as follows:

1. Small percentages of boron added to pure iron and melted in vacuo have a double effect upon the iron, since part of it reduces the iron oxide present, and the remainder combines with the iron.

2. Small additions of boron to iron have a slightly beneficial effect upon the magnetic properties, probably on account of the reduction of iron oxide, which more than offsets the effect of the combined boron. The beneficial effect in the present case reaches a maximum with additions of 0.05 percent B_7O or 0.4 percent B_7O-flux and ceases as soon as the amount of combined boron becomes measurable, which occurs with the addition of 0.1 percent B_7O or 0.75 percent B_7O-flux.

3. Boron added in a sufficient amount to leave a measurable quantity combined with the iron has a decidedly detrimental effect upon the magnetic properties of the iron.

4. Boron increases the specific electrical resistance of iron by 0.62 microhms per 0.1 percent of boron combined with the iron.

5. The effect of boron upon the mechanical properties of iron is, in general, similar to that of carbon. It raises the elastic limit and increases the ultimate strength, at the same time decreasing the toughness.

The addition of boron has also been used to render austenitic chromium-nickel steels hardenable by heat treatment. Boron alloys of very low carbon content show no susceptibility to precipitation hardening; with higher carbon, susceptibility to precipitation hardening is reduced by lowering the nickel or raising the chromium content. The precipitation is controlled by carbon content. The hardening constituent is a boride-carbide solid solution. Precipitation of this phase may have a direct hardening effect but may also function by depriving the austenite of its stabilizing elements and so inducing transformation to martensite on slow cooling or reheating. Cornelius(79) showed that the temper hardening of the low-carbon austenitic steels containing 8 percent or less of nickel is due solely to the formation of martensite, but when the carbon is higher

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the martensite formation may be preceded by true precipitation hardening. Even so, the temper hardening by boron of the chromium-nickel austenitic steels is held to be primarily due to martensite formation when the nickel does not exceed 8 percent.

Wasmuht(63) attributed the temper hardening of austenitic chromium-nickel steels containing boron to modification of the solubility relations of boron in iron brought about by the presence of nickel and chromium. Cornelius(79) believed that the temper hardening observed by Wasmuht was due mainly to the formation of martensite.

In 1932 Bennek and Schafmeister(65) published as their conclusions the fact that the austenitic structure of 18-8 steel was altered by beryllium, boron, and titanium. They found that the toughness of this steel was decreased, while resistance to corrosion was also decreased with increase in these elements and with increase in hardening.

Boron has been suggested as a surface-hardening element for steel. Chiyevskii(133) drilled cubes of soft iron in the center to about one-half their length and filled the holes with fine amorphous boron or with ferroboron. The holes were closed with stoppers of soft iron, and the stoppers were pressed down hard to compress the powdered contents of the cavity. The samples were then heated at 950° C. for 2 hours. It was found that the boron penetrated into the iron to a depth of 1 mm., and a hard layer was obtained. Powdered ferroboron proved more suitable than amorphous boron.

Campbell and Fay(135) found that boron penetrates a low-carbon steel in much the same manner as does carbon under similar conditions, but the boron-hardened steels show marked differences in their response to heat treatment and are never as hard as steels containing an equivalent quantity of carbon. They found that nitrogen is much more readily absorbed by a boron steel than by a carbon steel, this increase in absorptive power being due to formation of boric nitride at temperatures above that at which iron and nitrogen unite to form a stable nitride. Boron steels thus nitrified show those properties that would be expected in a steel of high nitrogen content, that is, extreme brittleness and a marked tendency toward exfoliation and chipping.

Special Addition Agents

The most outstanding use of boron in iron and steel, however, has been in special alloy addition agents. Among the first such special agents commercially available was Grainal, offered by the Vanadium Corp. of America. Several such special addition agents were available to the trade in 1942. A committee of the American Iron and Steel Institute(89) reported the following nominal compositions:

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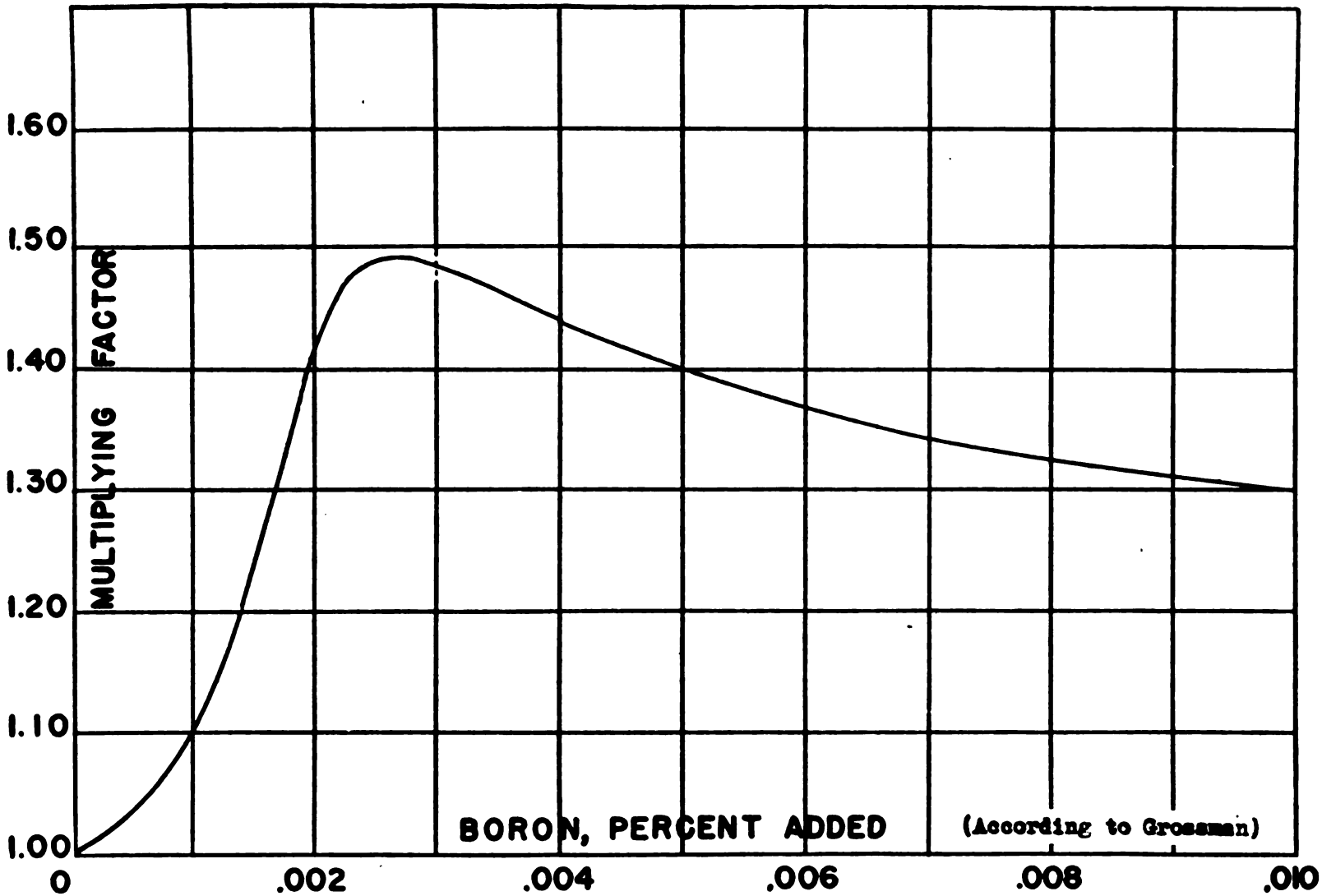

FIGURE 2.- Multiplying factor for calculating effect of boron on hardenability.

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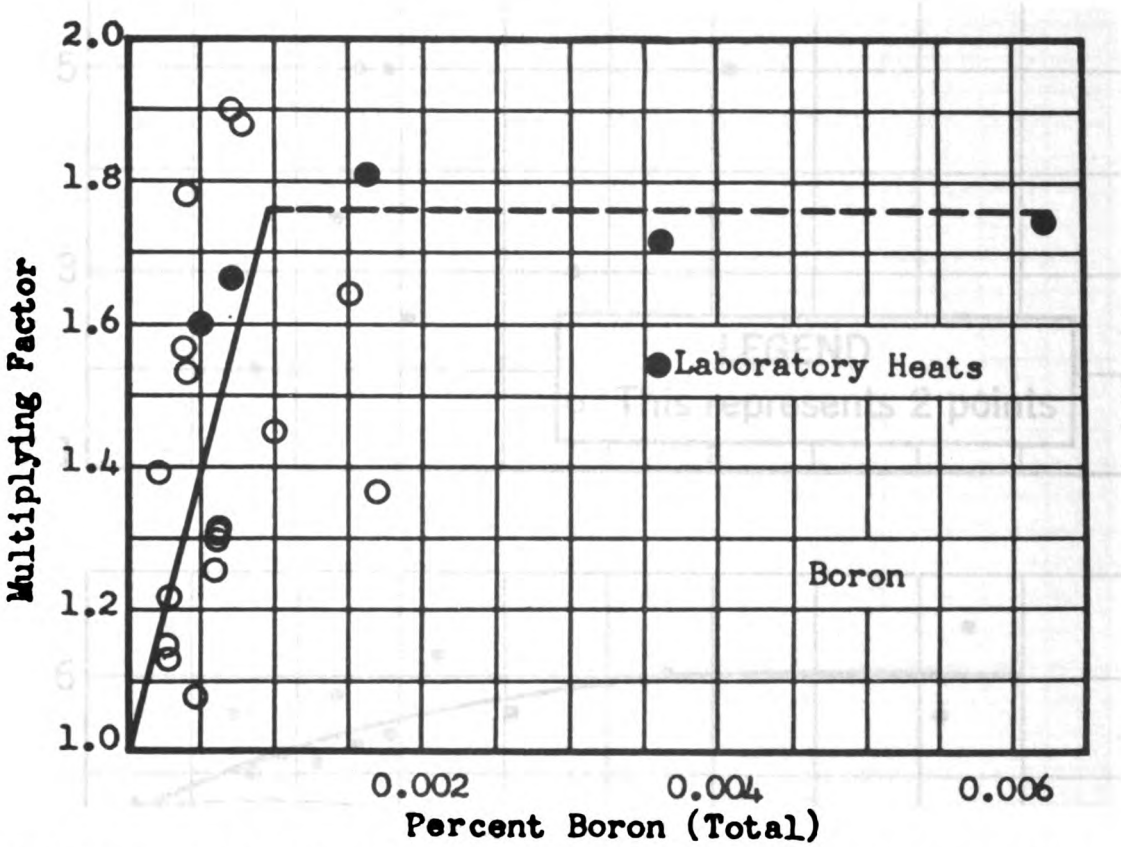

FIGURE 3.- Multiplying factor for boron (total), according to Crafts and Lamont.

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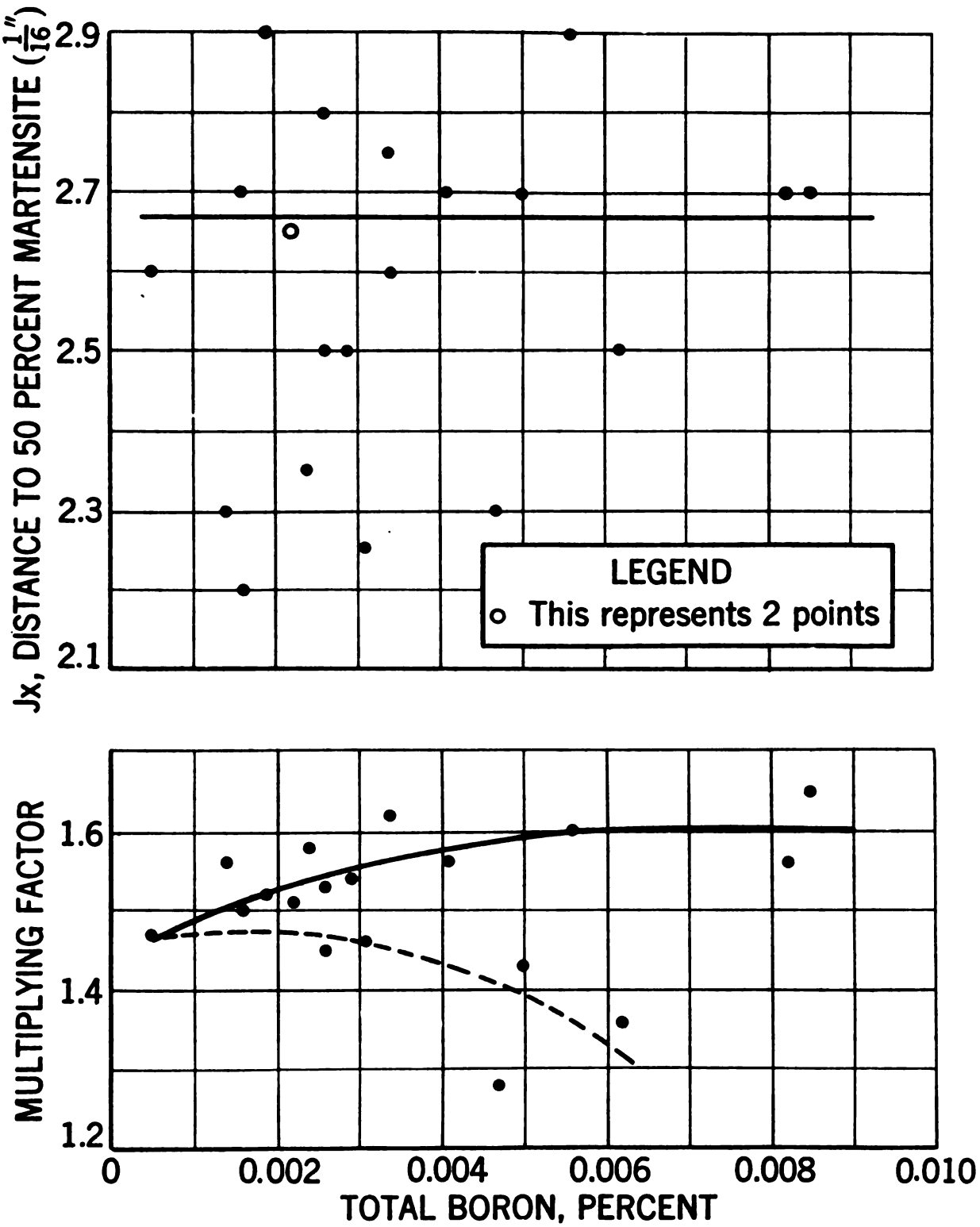

FIGURE 4.- Comparison of Jx and M. F. for boron steels of similar analyses.

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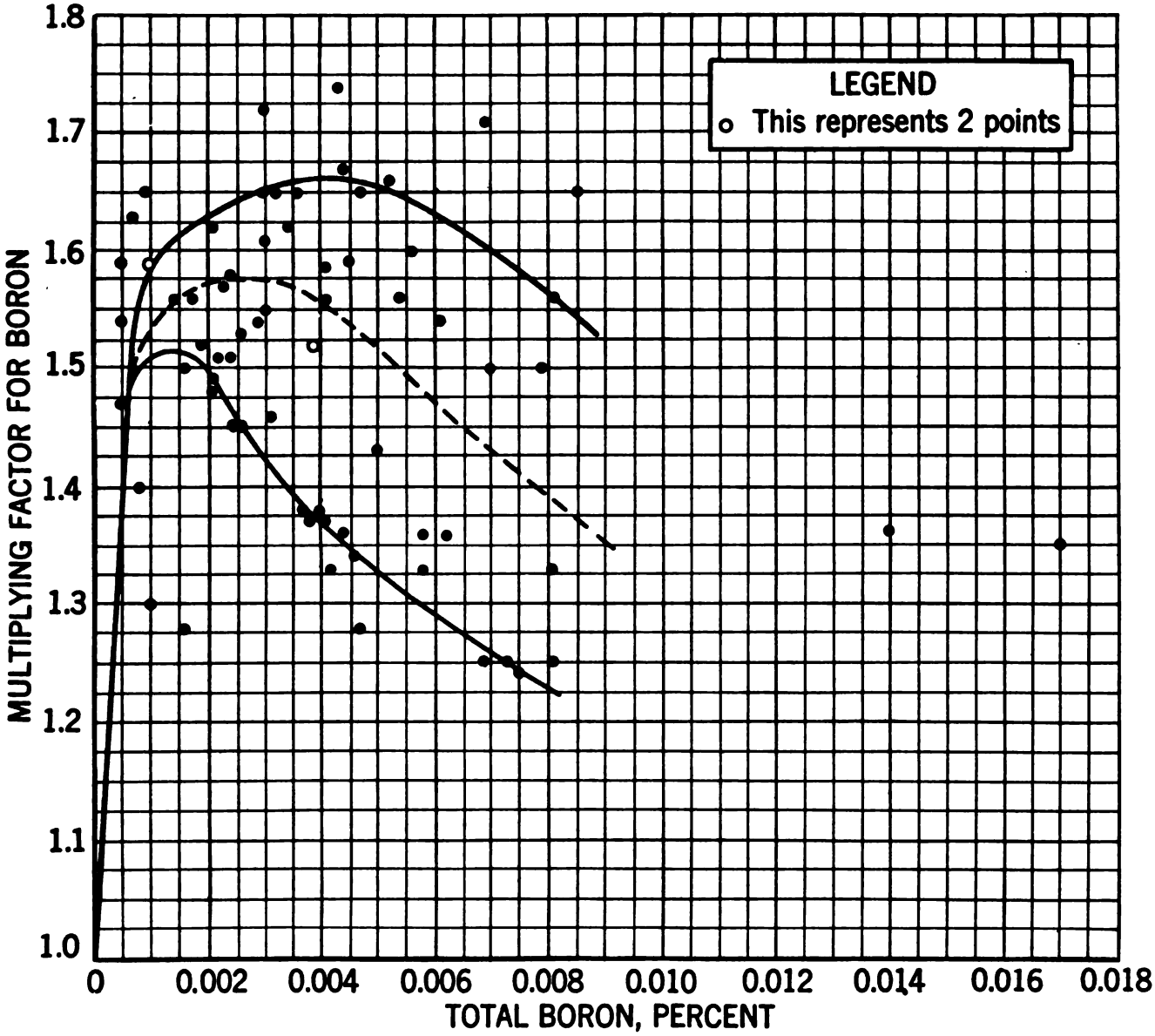

FIGURE 5.- Effect of boron on hardenability of steel.

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Alloy designation	Chemical composition, percent							
	Al	B	Ca	Mn	Si	Ti	Zr	Fe
1	7.0	0.5	10.0	-	35.0/40.0	10.0	4.0	Bal.
2	-	10.0/12.0	-	-	3.0	-	-	Bal.
3	10.0/20.0	1.0/2.0	-	15.0/25.0	20.0/30.0	10.0/20.0	-	Bal.
4	13.0	.5	-	8.0	-	20.0	4.0	Bal.

Table 1 is a current list indicating the manufacturers of the alloys, the first column being the commercial designation and the second the Corbett and Williams(125) designation.

The function of the boron in these alloys has been the subject of some difference of opinion. With the advent of the Grossmann(87) system of calculating hardenability it appeared possible to assign to boron an effect of the same type as that found for other steel alloying elements but of much greater magnitude. This effect is noticeable with very small quantities of boron.

Based on the addition of boron to a steel of known hardenability, Grossmann obtained the data in figure 2 between the relation of added boron and the multiplying factor.

For purposes of comparison, multiplying factors for other alloying elements as determined by Grossmann are given in the following table:

Elements	Multiplying factor
Manganese (to 1.7 percent)	1+(4.8) (percent Mn)
Manganese (above 1.7 percent)	1+6.0 (percent Mn-0.55)
Silicon	1+(0.67) (percent Si)
Aluminum	1+(0.93) (percent Al)
Nickel (to 3.2 percent)	1+(0.74) (percent Ni)
Nickel (above 3.2 percent)	1+(1.5) (percent Ni-1.63)
Chromium	1+(2.16) (percent Cr)
Molybdenum	1+(2.53) (percent Mo)
Zirconium	1+(2.53) (percent Zr)
Vanadium (to 0.25 percent)	1+(1.73) (percent V)
Titanium (to 0.11 percent)	1+(5.58) (percent Ti)
Boron (to 0.001 percent)	1+(790) (percent B)

Crafts and Lamont(117) found that the Grossmann multiplying factor for boron increased with the total boron content of the steel (0.30 to 0.55 percent carbon) up to 1.76 at slightly less than 0.0010 percent boron, and then the factor was either constant or decreased slightly. Their results are given in figure 3. In 1945 the Bureau of Mines undertook to check the effect of boron in steel, using a number of special addition agents, as well as ferroboron, manganese-boron, boric acid, and borax. The work of Corbett and Williams(125) in the Bureau laboratories indicates that a steel containing 0.52-0.63 percent Mn, 0.56-0.65 percent C, and 0.20-0.35 percent Si, fully deoxidized with ferrosilicon, will take up enough boron from any reduced or oxidic form to give a very large if not fully constant effect on hardenability. Their results are shown in figures 4 and 5.

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TABLE 1.- Composition of commercial boron-containing agents
Individual analyses as recorded in the literature (analyses supplied by manufacturer given in parentheses)

Agents	Designation	Composition, percent										Manufacturer
		B	Ti	V	Zr	Al	Si	Mn	C	Fe	Other	
Silvaz 3 alloy	Silvaz	(0.55-0.75) 0.5	(9-11) 10	(9-11) 10	(5-7) 6	(5-7) 6	(35-40) 37			bal.		Electro Metallurgical Co.
Silcaz 3 alloy	Silcaz	(0.55-0.75) 0.5	(9-11) 10		(3-5) 4	(6-8) 7	(35-40) 37			bal.	(Ca9-11) Ca 10	Electro Metallurgical Co.
Bortam	Bortam	(1.5-1.9) 1.7	(16-18) 17			(13-15) 14	(20-22) 21	(21-24) 22	(<1)	(bal.) bal.		Titanium Alloy Mfg. Co.
Carbortam	Carbortam	(0.90-1.15) 1.0	(15-17) 16			(1-2) 1.5	(2.5-3.0) 3	(0.1-0.2)	(6.5-7.5) 7	(69-70) bal.	(Cr. 0.10-0.20 S0.025-0.035 P0.0025-0.0035)	Titanium Alloy Mfg. Co.
Borosil	Borosil	(3-4) 3.5					(40) 42			(bal.) bal.		Ohio Ferro Alloys Corp.
Manganese-boron alloy	MnB	(15-20) 20.8					(<1.5)	(75 approx.) bal.	(<3.0)	(<5)		Electro Metallurgical Co.
Nickel-boron alloy	NiB	(15-18) 10.7				(<1)	(<1.5)		(<0.5)	(<3.00)	(Ni bal.) Ni bal.	Electro Metallurgical Co.
Grainal No. 79	Grainal	(0.5)	(20)		(4)	(13)		(8)				Vanadium Corp. of America.
Vanadium Grainal No. 1	Grainal No. 1	(0.2)	(15)	(25)		(10)						Vanadium Corp. of America
Vanadium Grainal No. 6	Grainal No. 6	(0.2)	(20)	(13)		(12)						Vanadium Corp. of America
Ferro-boron	FeB	(10-14) 10.2					(4)		(<3) 0.70	(bal.) bal.		Molybdenum Corp. of America
Ferro-boron	FeB	(>17.50)				(<0.5)	(<1.5)		(<0.5)	(bal.)		Electro Metallurgical Co.
Fused boron trioxide glass	B_2O_3								0.3		B_2O_3 99	
Pyrobor	$Na_2B_4O_7$										$Na_2B_4O_7$ 100	

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The results of these investigations further indicate that the steels were originally fine-grained (7-8.5 P-F grain-size standard) and the grain size was unaffected by the boron additions.

As an average, Corbett and Williams point out that 0.003 percent boron exerts the same influence on hardenability as 263 times as much nickel, 90 times as much chromium, 40 times as much manganese, or 77 times as much molybdenum.

It should be noted that the fairly constant and reproducible effect of boron, regardless of the method of addition, is based on its use according to a steel-making practice which produces a fine grain.

The very high multiplying factor of boron up to 0.0025 percent and its small or reverse effect beyond that point, indicates a different mechanism of action than in the case of manganese, chromium, molybdenum and other alloying elements.

Even in the case of these elements, recent investigations by Holloman and Jaffe(128) and also by Brophy and Miller(123) have indicated that at least two hardening effects are involved. Holloman and Jaffe report that in some steels the formation of bainite restricts the formation of martensite, while in others pearlite is the limiting factor. We are inclined to agree with these investigators on the following statement:

> Information available on the elements boron, titanium, and vanadium is contradictory, and may indicate that the effects of these elements upon hardenability depend to some extent upon factors other than the amount of the element contained in the austenite.

If the effect of boron is secondary, we must use caution in attempting to apply to it the rules of hardenability established for elements whose effect is due to solubility in austenite. Such a secondary effect on hardenability is already known and fully recognized in austenitic grain-size control.

Although not entirely agreed upon, presumably fine-grained steels are shallower hardening because the increased "internal surface" provides more starting points for the austenitic transformations. Fine-grain is produced by deoxidation, particularly with excess aluminum, which, as suggested by Dean(131) may stabilize the foam cells formed by the gas-metal system at the time of solidification. In any case there is here involved a colloidal phenomenon. The problem in its most basic sense is to prevent the grain boundaries in a fine-grained steel from becoming starting points for austenitic transformation. We thus have the advantage of fine-grain and deep-hardening. The nature of the austenitic grain boundaries depends on deoxidation practice and addition agents. The addition of boron is useful in such practice, but the entire deoxidation technique and the boron addition must be considered as a whole. Empirical formulas for boron additions may therefore have merit which cannot be analyzed in terms of multiplying factors.

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The very large effect of boron on hardenability suggests a dispersion in the austenite rather than solution. The existence of a maximum at so low a percentage indicates the reaction of boron when present beyond a very small percentage with some other constituent of the steel. According to Tisdale(114), boron in excess of 0.003 percent may cause the formation of an envelope of iron-carbide, iron-boride solid solution around the grains.

According to Chandler and Bredig(132), the hardenability effect of boron, either alone or in combination with other elements, is neither an alloying effect in the usual sense of the word nor a compound-formation with nitrogen but appears to be the influence of a fluxing agent upon the particle size of nitrides of other elements, such as those of silicon, aluminum, titanium, and zirconium.

The work of the Bureau of Mines reported by Corbett and Williams indicates that carbon, silicon, and manganese all combine with the boron to increase the proportion of "insoluble" boron as revealed by analysis (tables 2 and 3). Table 2 also gives the efficiencies of the various boron-agents when added to steel. For convenience they may be listed as follows:

Addition agent	No. of heats	Range of efficiencies	Average efficiency
Ferroboron	29	49.3-130.0	79.5
Titanium boride	13	16.7-94.5	56.0
Siloaz	7	72.0-120.0	98.9
Manganese boron alloy .	7	66.2-87.7	78.0
Chromium-boron	6	48.4-100.5	72.5
Borosil	5	84.7-139.0	88.7
Bortam	5	21.3-55.7	38.5
Boron carbide	4	80.7-119.0	98.0
Silvaz	4	73.0-106.0	88.0
Carbortam	4	36.2-88.5	61.1
Nickel-boron alloy	3	76.7-98.5	88.6
C	2	49.0-50.0	49.5
F	1		58.1
G	1		32.0

In the above table the very wide variations in boron recovery should be noted. The accuracy of the analytical method used to determine boron at the particular level of boron content employed undoubtedly influences the boron recovery value. Figure 6 shows the effect of the carbon content of the steel on the percent of soluble boron. Similar curves (figs. 7 and 8) are obtained if the manganese or silicon content of the steel is plotted instead of the carbon content.

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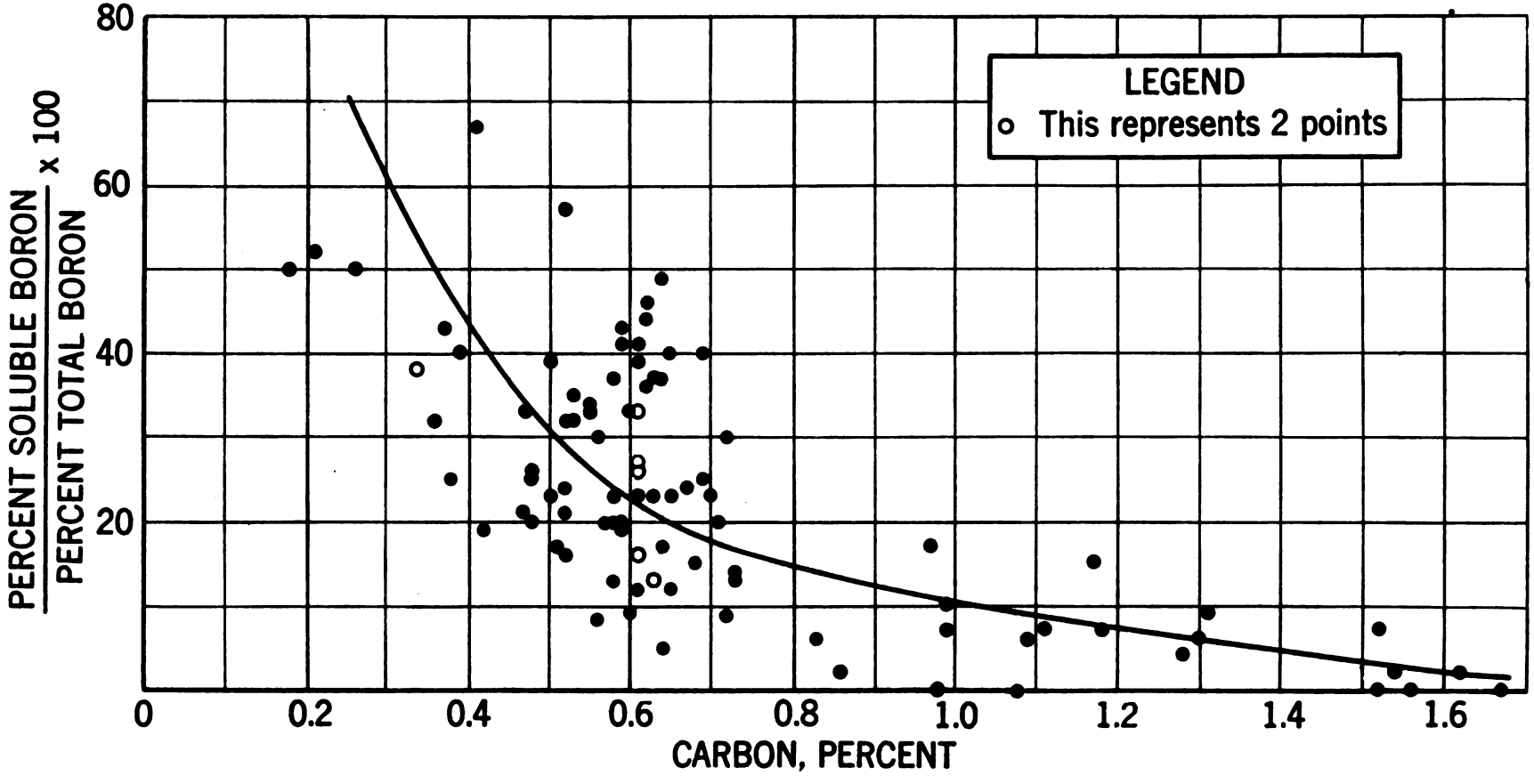

FIGURE 6.- Effect of carbon on percent of soluble boron.

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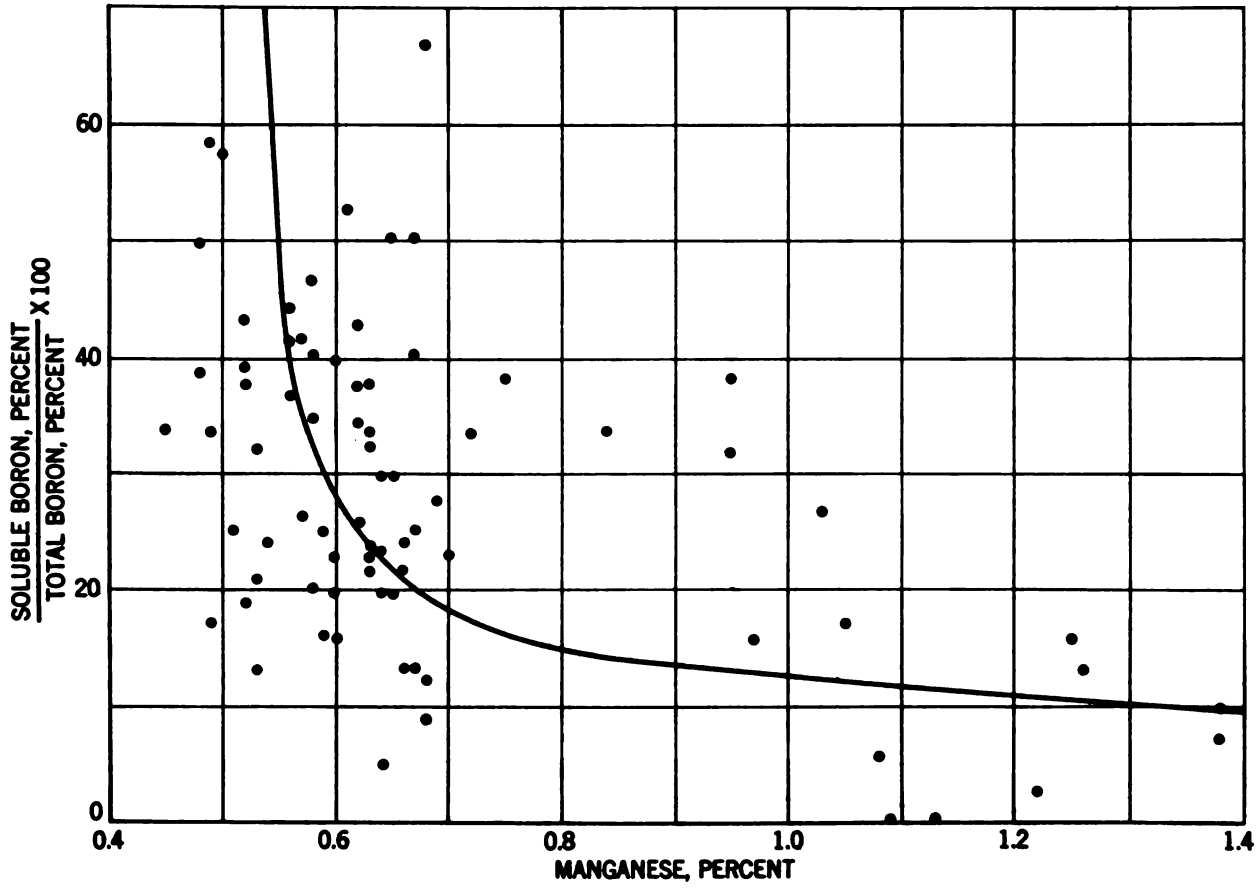

FIGURE 7.- Effect of manganese on percent of soluble boron.

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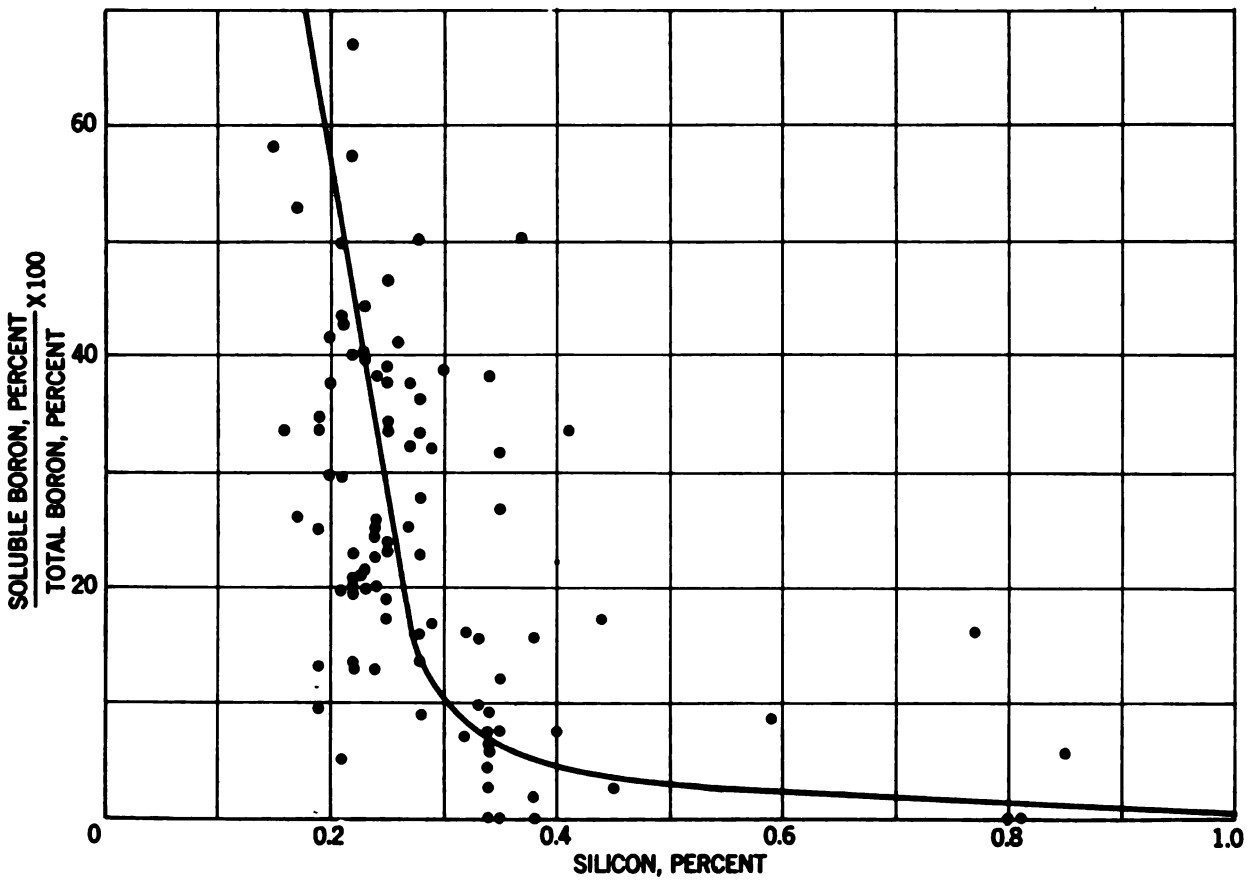

FIGURE 3.- Effect of silicon on percent of soluble boron.

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TABLE 2.- Experimental data

Heat No.	Chemical analysis, percent			Boron			Boron addition agent		Ingot weight, lb.	Efficiency of addition[1]	Percent soluble B. is of T.B.[2]	Grain size	J_x[3]	M. F. due to boron[4]
	C	Mn	Si	Soluble	Insoluble	Total	Designation	Percent added						
1..	0.56	1.72	0.59	0.0007	0.0074	0.0081	MnB	0.0100	5	-	8.6	-	-	-
2..	2.47	1.69	1.78	.0000	.0008	.0008	MnB	.0010	5	-	0	-	-	-
3..	1.52	1.13	.80	.0000	.0000	.0000	None	.0000	5	-	0	-	-	-
4..	1.08	.93	.81	.0000	.0012	.0012	MnB	.0020	5	-	0	-	-	-
5..	.83	1.08	.85	.0002	.0033	.0035	MnB	.0050	5	-	5.7	-	-	-
85/	.52	1.73	.77	.0013	.0068	.0081	FeB	.0050	5	-	16.0	8	13	1.25
9..	.36	.95	.35	.0013	.0028	.0041	6/FeB	.0050	15	-	31.7	8	-	-
10..	1.17	1.25	.38	.0010	.0054	.0064	7/FeB	.0050	15	-	15.6	8	-	-
11..	.98	1.09	.35	.0000	.0025	.0025	6/FeB	.0025	15	-	0	8	-	-
12..	.97	1.05	.44	.0018	.0088	.0106	6/FeB	.0100	15	-	17.0	8	-	-
13..	1.62	1.22	.45	.0002	.0081	.0083	6/BC	.0050	15	-	2.4	8	-	-
14..	1.11	1.38	.32	.0006	.0080	.0086	BC	.0082	14.5	101.2	7.0	8	-	-
165/	1.50	1.51	.35	.0003	.0036	.0039	6/MnB	.0050	12.7	66.2	7.7	6	-	-
17..	1.30	1.44	.34	.0002	.0046	.0048	MnB	.0050	14.0	87.7	6.4	6	-	-
18..	1.28	1.46	.34	.0002	.0044	.0046	7/MnB	.0050	14.1	86.0	4.4	8	-	-
19..	.99	1.38	.33	.0005	.0046	.0051	CrB	.0050	14.8	100.5	9.8	7	-	-
20..	1.31	1.45	.34	.0004	.0040	.0044	6/CrB	.0050	14.4	84.6	9.1	6	-	-
21..	1.09	1.47	.34	.0003	.0048	.0051	$Na_2B_4O_7$	10 gr.	13.1	-	5.9	8	-	-
22..	1.18	1.43	.34	.0003	.0038	.0041	$Na_2B_4O_7$	5 gr.	13.7	-	7.3	8	-	-
23..	.86	1.40	.34	.0003	.0120	.0123	B_2O_3	10 gr.	13.7	-	2.4	9	-	-
24..	1.67	1.39	.34	.0000	.0025	.0025	TiB	0.0050	13.7	45.7	0	8	-	-
25..	.99	1.65	.40	.0002	.0025	.0027	6/TiB	.0050	11.6	41.8	7.4	9	-	-
26..	1.56	1.49	.38	.0000	.0037	.0037	TiB	.0050	12.8	63.2	0	8	-	-
27..	1.54	1.64	.38	.0001	.0052	.0053	6/TiB	.0050	10.4	73.6	1.9	8	-	-
28..	.73	1.26	.19	.0003	.0020	.0023	TiB	.0020	12.3	94.5	13.0	8	-	-
29..	.72	1.30	.19	.0003	.0029	.0032	TiB	.0040	14.0	74.7	9.4	8	5.0	1.09
30..	.60	.84	.25	.0013	.0026	.0039	TiB	.0060	15.0	65.0	33.3	8	3.0	1.22
31..	.61	1.03	.35	.0020	.0055	.0075	TiB	.0080	11.75	73.5	26.7	8	3.6	1.08
32..	.68	.97	.33	.0008	.0044	.0052	TiB	.0100	13.75	47.6	15.4	8	2.8	.94
33..	.34	.95	.34	.0008	.0013	.0021	FeB	.0010	9.25	130.0	38.1	7	3.8	1.49
34..	.34	.75	.24	.0008	.0013	.0021	FeB	.0020	12.6	88.3	38.1	8	2.5	1.62
35..	.48	.70	.22	.0006	.0024	.0030	FeB	.0030	11.5	76.7	20.0	8	2.8	1.55
36..	.21	.61	.17	.0022	.0020	.0042	FeB	.0050	14.5	81.3	52.4	8	8/	-
37..	.18	.65	.28	.0029	.0029	.0058	FeB	.0070	13.6	75.3	50.0	8	8/	-
38..	.37	.62	.21	.0023	.0031	.0054	FeB	.0090	12.5	50.0	42.6	8	1.8	1.56
39..	.53	.63	.27	.0008	.0017	.0025	$Na_2B_4O_7$	2 gr.	14.0	-	32.0	8	2.5	1.45
40..	.63	.63	.24	.0014	.0048	.0062	$Na_2B_4O_7$	4 gr.	13.0	-	22.6	8	2.5	1.36
41..	.50	.64	.25	.0009	.0030	.0039	B_2O_3	2 gr.	13.5	-	23.0	8	2.6	1.52
42..	.47	.66	.23	.0013	.0048	.0061	B_2O_3	4 gr.	13.5	-	21.3	8	2.5	1.54
43..	.39	.67	.23	.0002	.0003	.0005	FeB	0.0005	15.0	100.0	40.0	7.5	2.5	1.59
44..	.48	.67	.24	.0002	.0006	.0008	FeB	.0010	13.25	70.7	25.0	7	2.6	1.40
45..	.41	.68	.22	.0016	.0008	.0024	FeB	.0020	14.25	114.0	66.7	5	3.5	1.51
46..	.38	.59	.19	.0008	.0024	.0032	FeB	.0050	14.75	62.9	25.0	8.5	1.75	1.65
47..	.47	.63	.19	.0015	.0030	.0045	FeB	.0070	16.0	68.6	33.3	8	2.4	1.59
48..	.57	.67	.69	-	-	2/.0051	Silcaz	.0050	12.9	87.5	-	8.5	3.4	.98
49..	.49	.67	.31	.0003	.0018	.0021	Bortam	.0050	14.1	39.5	14.3	8	2.4	1.40
50..	.60	.67	.23	.0018	.0018	.0036	Carbortam	.0050	13.25	63.6	50.0	8	2.3	1.27
51..	.65	.68	.35	.0009	.0066	.0075	Borosil	.0050	13.1	139.0	12.0	8	2.7	1.24
52..	.73	.90	.28	.0007	.0044	.0051	CrB	.0050	7.1	48.4	13.7	8	-	-
53..	.48	.62	.24	.0010	.0029	.0039	MnB	.0050	15.6	81.3	25.6	8	2.3	1.52
54..	.45	.64	.54	-	-	2/.0040	Silvaz	.0050	14.6	78.0	-	8	3.7	1.04
55..	.57	.64	.23	.0009	.0037	.0046	NiB	.0058	14.5	76.7	19.6	8	2.25	1.34
56..	.65	.63	.24	.0011	.0036	.0047	FeB	.0050	10.5	65.8	23.4	8	2.3	1.28
57..	.47	.63	.33	-	-	2/.0053	Silvaz	.0050	15.0	106.0	-	8	3.2	1.04
58..	.52	.60	.36	-	-	2/.0052	Silcaz	.0050	14.5	100.0	-	9	2.9	1.13
59..	.75	.71	.26	.0008	.0023	.0031	Bortam	.0050	12.0	49.6	25.8	8	1.8	.95
60..	.67	.63	.10	.0008	.0009	.0017	Carbortam	.0050	16.0	36.2	47.0	8	1.8	1.21
61..	.55	.62	.25	.0014	.0027	.0041	CrB	.0050	10.5	57.3	34.1	8	2.2	1.37
62..	.36	.49	.15	.0025	.0018	.0043	Borosil	.0050	14.75	84.7	58.2	8	1.4	1.74
63..	.42	.65	.22	.0007	.0029	.0036	MnB	.0050	15.0	72.0	19.4	8	2.5	1.65
64..	.58	.66	.22	.0009	.0060	.0069	BC	.0080	14.0	80.7	13.0	8	2.0	1.25
65..	.43	.65	.39	-	-	2/.0022	Silcaz	.0025	15.0	88.0	-	8.5	1.25	.96
66..	.53	.58	.19	.0018	.0034	.0052	B_2O_3	5 gr.	13.4	-	34.6	8	2.6	1.66
67..	.52	.63	.23	.0015	.0055	.0070	FeB	0.0120	16.0	62.2	21.3	8	2.5	1.50

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TABLE 2.- Experimental data (Cont'd)

Heat No.	Chemical analysis, percent						Boron addition agent		Ingot weight, lb.	Efficiency of addition 1/	Percent soluble B. is of T.B. 2/	Grain size	J_x 3/	M. F. due to boron 4/
	C	Mn	Si	Boron Soluble	Boron Insoluble	Boron Total	Designation	Percent added						
68..	0.64	0.64	0.21	0.0004	0.0077	0.0081	FeB	0.0160	14.6	49.3	4.9	8	2.4	1.33
69..	.58	.70	.22	.0030	.0110	.0140	FeB	.0170	14.3	78.6	22.8	8	2.6	1.36
70..	.56	.65	.21	.0050	.0120	.0170	FeB	.0200	12.6	71.5	29.4	7	2.6	1.35
71..	.59	.52	.21	.0006	.0008	.0014	FeB	0020	13.6	63.5	43.0	8	2.3	1.56
72..	.52	.66	.25	.0005	.0016	.0021	FeB	0015	11.1	104.0	23.8	8	2.6	1.48
73..	.64	.48	.21	.0034	.0035	.0069	FeB	.0080	13.4	77.2	49.5	8	2.6	1.71
74..	.69	.51	.27	.0001	.0004	.0005	TiB	.0030	15.0	16.7	25.0	8	2.7	1.54
75..	.70	.60	.28	.0010	.0034	.0044	FeB	.0030	12.0	117.5	22.7	8	2.7	1.36
76..	.57	.47	.13	.0007	.0002	.0009	Bortam	.0030	13.0	26.0	78.0	8	1.9	1.65
77..	.56	.55	.23	.0007	.0008	.0017	Carbortam	.0030	14.8	56.1	41.0	8	2.4	1.56
78..	.61	.53	.22	.0007	.0027	.0034	FeB	.0040	15.4	87.3	20.6	8	2.6	1.62
79..	.61	.59	.32	.0008	.0042	.0050	FeB	.0060	15.2	84.5	16.0	8	2.7	1.43
80..	.60	.53	.34	-	-	9/.0028	Silvaz	.0030	15.3	95.2	-	8	2.7	1.13
81..	.58	.52	.25	.0009	.0015	.0024	CrB	.0030	15.0	80.0	37.5	8	2.35	1.58
82..	.62	.56	.28	.0008	.0014	.0022	MnB	.0030	14.75	72.3	36.3	8	2.65	1.51
83..	.62	.58	.25	.0012	.0014	.0026	BC	.0030	15.8	91.1	46.2	8	2.5	1.45
84..	.62	.56	.23	.0036	.0046	.0082	FeB	.0100	15.2	82.8	44.0	8	2.7	1.56
85..	.61	.52	.25	.0033	.0052	.0085	FeB	.0140	15.3	61.8	39.0	8	2.7	1.65
86..	.69	.60	.23	.0023	.0035	.0058	FeB	.0080	15.0	72.6	39.7	8	2.5	1.36
87..	.71	.58	.24	.0008	.0032	.0040	FeB	.0050	14.5	77.5	20.0	8	2.6	1.38
88..	.65	.58	.22	.0002	.0003	.0005	FeB	.0008	15.0	62.5	40.0	8	2.6	1.47
89..	.52	.53	.29	.0015	.0032	.0047	Borosil	.0050	15.3	96.0	31.9	8	2.5	1.65
90..	.58	.52	.32	-	-	9/.0022	Silcaz	.0020	15.0	110.0	-	8	2.65	1.47
91..	.60	.55	.35	-	-	9/.0034	Silcaz	.0030	15.25	115.0	-	8	2.75	1.28
92..	.61	.49	.28	.0010	.0020	.0030	$Na_2B_4O_7$	4 gr.	17.5	-	33.3	8	2.6	1.65
93..	.61	.45	.16	.0010	.0020	.0030	B_2O_3	3 gr.	17.0	-	33.3	8	1.9	1.61
94..	.59	.52	.25	.0003	.0013	.0016	$Na_2B_4O_7$	3 gr.	16.5	-	18.8	8	2.2	1.50
95..	.50	.48	.30	.0017	.0027	.0044	NiB	0.0050	15.5	90.6	38.6	8	2.2	1.67
96..	.61	.56	.26	.0023	.0033	.0056	BC	.0050	16.0	119	41.1	8	2.9	1.60
97..	.67	.54	.24	.0019	.0060	.0079	FeB	.0080	14.6	96.1	24.1	8	2.6	1.50
98..	.64	.73	.29	.0007	.0035	.0042	MnB	.0050	14.4	80.7	16.7	8	3.2	1.33
99..	.26	.67	.37	.0015	.0015	.0030	C	.0050	12.5	50.0	50.0	8	2.1	1.72
100..	.59	.57	.20	.0012	.0017	.0029	F	.0050	15.0	58.1	41.4	8	2.5	1.54
101..	.63	.63	.20	.0006	.0010	.0016	G	.0050	15.0	32.0	37.5	8	2.1	1.28
102..	.64	.62	.27	.0090	.0150	.0240	FeB	.0300	13.5	72.1	37.5	8	10/	-
103..	.61	.69	.28	.0016	.0042	.0058	NiB	.0050	12.75	98.5	27.5	8	2.75	1.33
104..	.61	.60	.28	.0003	.0016	.0019	TiB	.0040	15.5	49.2	15.8	8	2.9	1.52
105..	.63	.53	.24	.0004	.0027	.0031	CrB	.0050	15.5	64.0	12.9	8	2.25	1.46
106..	.60	.68	.28	.0003	.0034	.0037	TiB	.0080	15.5	44.0	8.8	8	2.85	1.38
107..	.63	.67	.22	.0005	.0033	.0038	$Na_2B_4O_7$	2 gr.	15.0	-	13.2	8	2.7	1.37
108..	.52	.50	.22	.0004	.0003	.0007	TiB	0.0020	16.5	38.4	57.2	8	2.1	1.63
109..	.72	.64	.20	.0021	.0052	.0073	B_2O_3	4 gr.	15.0	-	29.8	8	2.4	1.25
110..	.58	.60	.21	.0008	.0033	.0041	B_2O_3	2 gr.	15.5	-	19.5	8	2.7	1.56
111..	.61	.64	.25	.0002	.0015	.0017	Bortam	0.0030	14.75	55.7	11.8	8	2.6	1.39
112..	.59	.52	.18	.0002	.0008	.0010	Bortam	.0050	16.0	21.3	20.0	8	2.3	1.59
113..	.55	.72	.41	.0003	.0007	.0010	Borosil	.0030	13.5	39.0	33.3	8	2.9	1.30
114..	.62	.57	.17	.0006	.0017	.0023	C	.0050	16.0	49.0	26.1	8	2.6	1.57
115..	.61	.62	.23	.0006	.0020	.0026	Carbortam	.0030	15.25	88.5	23.1	8	2.8	1.53
116..	.51	.49	.25	.0007	.0034	.0041	Borosil	.0050	15.5	85.0	17.1	8	2.5	1.59
117..	.65	.65	.49	-	-	9/.0038	Silcaz	.0050	14.2	72.0	-	8	3.3	1.15
118..	.74	.60	.39	-	-	9/.0038	Silvaz	.0050	14.4	73.0	-	8	2.6	.80
119..	.58	.59	.41	-	-	9/.0035	Silcaz	.0030	15.5	120.0	-	8	3.7	1.29

1/ Efficiency of boron addition is equal to

$$\frac{\text{Percent total boron as found by chemical analysis}}{\text{Percent added boron}\left(\frac{15}{\text{Actual ingot weight}}\right)} \times 100$$

because the boron addition was based upon an ingot weight of 15 pounds, which was seldom obtained.

2/ $\frac{\text{Percent soluble boron}}{\text{Percent total boron}} \times 100$.

3/ J_x is the distance, in sixteenths, along side of Jominy bar from the end-quenched face to the position of 50 percent martensite.

4/ Multiplying factor due to boron as found by calculation.

5/ Heat numbers 6, 7, and 15 were lost.

6/ Envelope containing the boron addition agent was plunged into molten steel bath by means of an iron wire.

7/ The boron addition agent was placed in the end of an iron rod that had been drilled for this purpose. The end of the rod was then closed by an iron plug. When this end was plunged into the steel bath and stirred, it dissolved and thus introduced the boron into the melt.

8/ Carbon too low for standard Jominy hardenability test.

9/ Percentage of boron determined by the distillation method instead of the colorimetric method.

10/ Ingot was hot-short; Jominy bar could not be forged.

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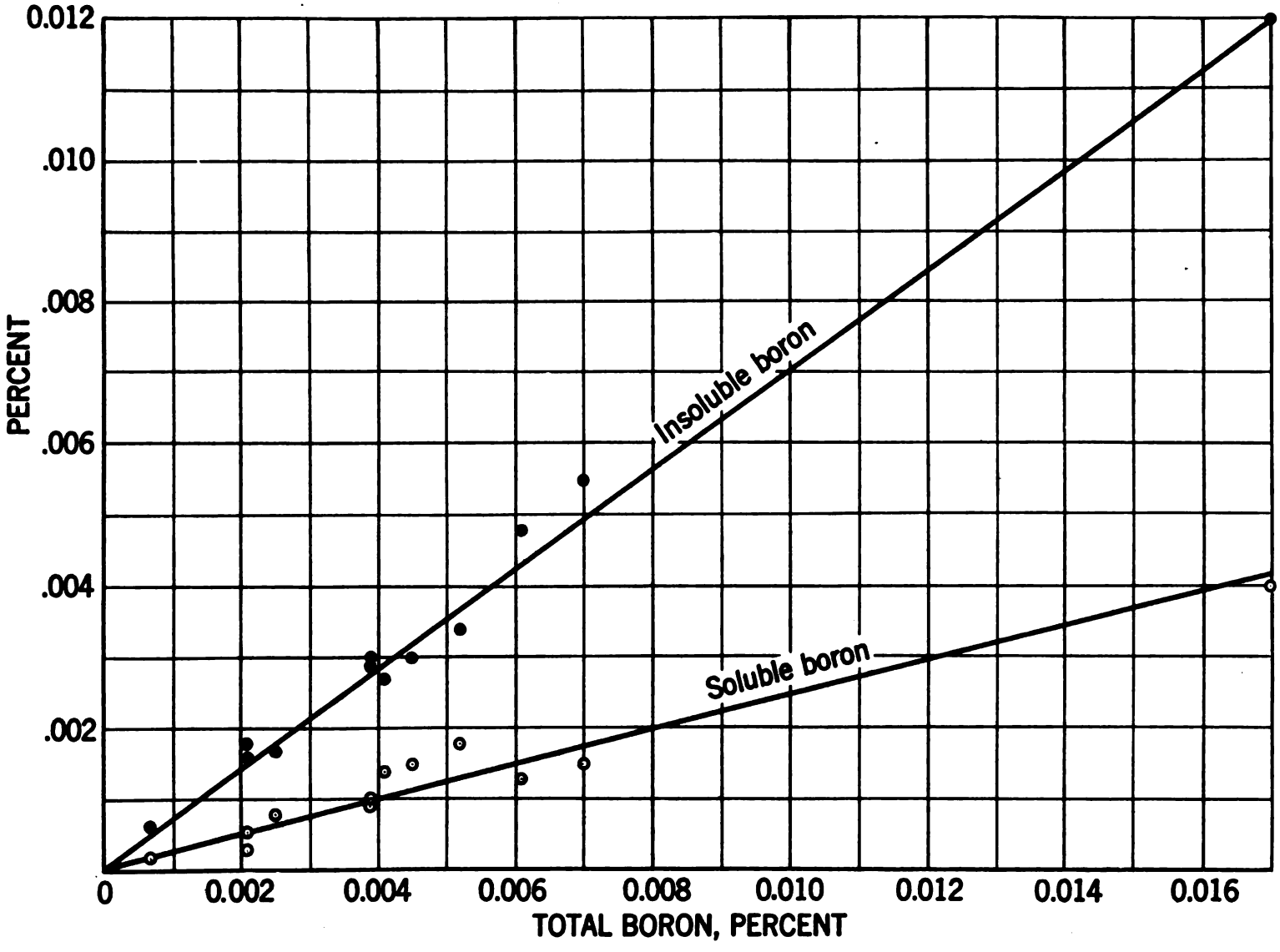

FIGURE 9.- Change in soluble and insoluble boron with change of total boron for boron steels of similar analyses.

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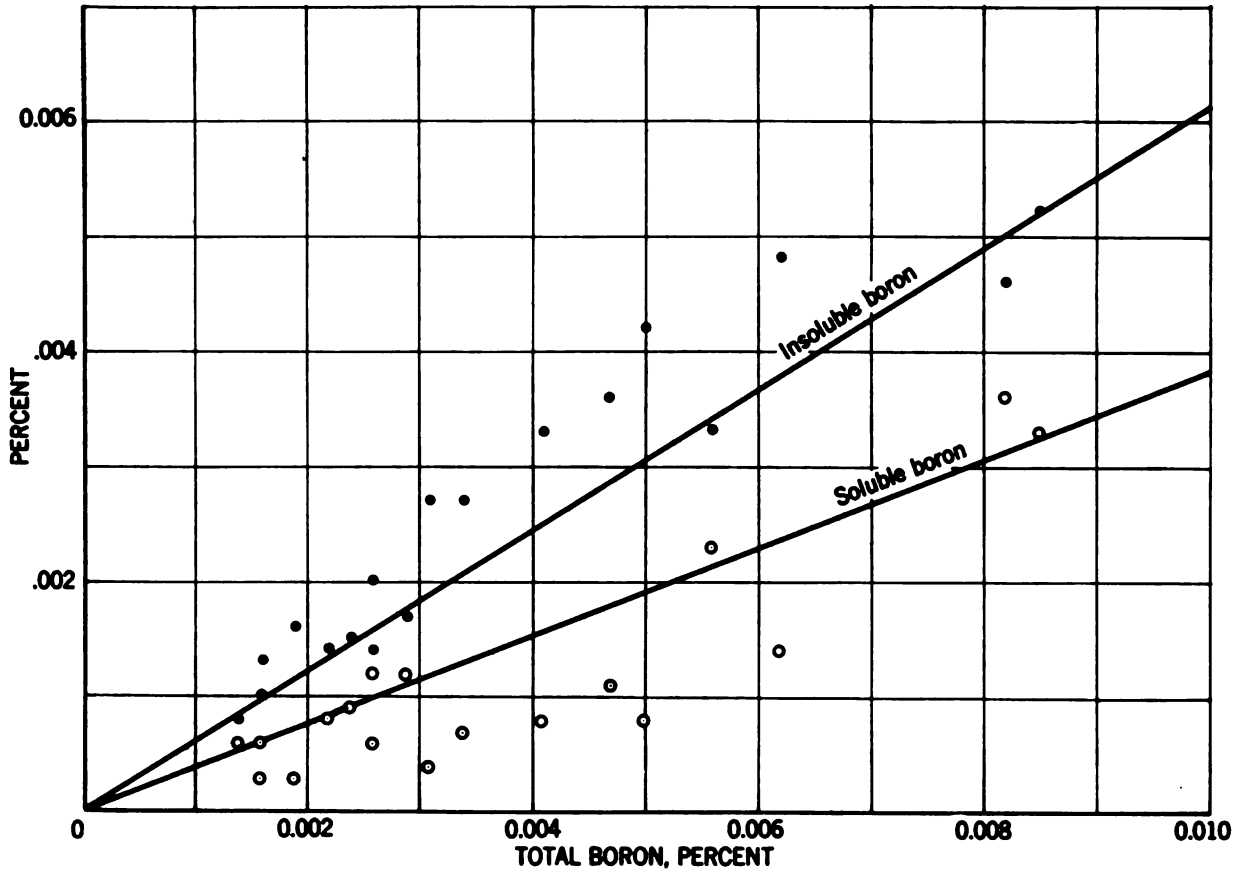

FIGURE 10.- Change in soluble and insoluble boron with change in total boron for boron steels of similar analyses.

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TABLE 3. - Supplement to table 2

Heat No.	Percent total Ti	M. F. due to Ti	Percent total V	M. F. due to V	M. F. due to "residuals"	General M. F. for cal.
48	0.065	1.36	-	-	1.07	1.46
54	.074	1.42	0.080	1.14	1.07	1.73
57	.074	1.42	.092	1.16	1.07	1.76
58	.094	1.52	-	-	1.07	1.63
65	.035	1.19	-	-	1.07	1.27
80	.044	1.25	.061	1.105	1.07	1.48
90	.016	1.09	-	-	1.07	1.17
91	.037	1.20	-	-	1.07	1.28
117	.029	1.16	-	-	1.07	1.24
118	.058	1.32	.087	1.15	1.07	1.62
119	.054	1.30	-	-	1.07	1.39

These investigations showed further that the insoluble boron increased more rapidly with the total boron than the soluble boron, indicating that beyond a minimum amount of soluble boron there is an increasing tendency of the boron to react with the constituents of the steel. The soluble boron increases but little beyond the point of maximum hardenability at 0.0025 percent total boron. The results for the relationship between total boron and soluble and insoluble boron for steels within the composition range:

C, percent	Mn, percent	Si, percent
0.47/0.57	0.58/0.67	0.19/0.31

are given in figure 9.

Figure 10 shows that a similar result is obtained for the steels of the group which fall within the range:

C, percent	Mn, percent	Si, percent
0.58/0.65	0.52/0.63	0.20/0.35

Corbett and Williams believed that both soluble and insoluble boron affect the hardenability. Attributing the hardenability to the "soluble" boron qualitatively explains the maximum in the relationship of multiplying factor to total boron content.

Comstock(124) has reported that the hardenability for "soluble" titanium is very high, approaching that of boron, but that in most steels the decrease in hardenability due to carbide-forming action is much more important. The secondary effects of boron may similarly blanket the established effect of "soluble" boron on hardenability.

Grange and Garvey(126) compared the hardenability of four series of plain carbon steels containing 0.40, 0.52, 0.63, and 0.75 percent of carbon, respectively, each series prepared by adding graded amounts of boron to

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adjacent ingots. It is shown that the increase in hardenability that results from addition of the optimum amount of boron decreases with increasing carbon content; the implication is that boron will not increase the hardenability of hypereutectoid steel. Other factors, such as time at high temperature and austenitic grain size, were shown by Grange and Garvey to influence the hardenability of boron-treated steels in a way quite different from their influence upon boron-free steel of comparable composition. A summary of their work follows:

1. In all these steels hardenability is increased by boron, although it is also raised somewhat by the addition of Grainal without boron. The increase due to boron is greater the lower the carbon, at least to 0.4 percent; and it appears to approach zero in hypereutectoid carbon steels.

2. The increase in hardenability produced by boron is greatest when the austenitizing temperature is 1550° to 1600° F. (845° to 870° C.), as ordinarily used in practice; it becomes gradually less for higher austenitizing temperatures and may approach zero when the latter is about 2,000° F. (1095° C.).

3. In a given steel, the increase in hardenability roughly parallels, but does not correlate well with, the percentage of boron as determined by chemical analysis of the steel. It appears, however, that, as others have reported, as little as 0.001 percent boron may suffice to develop the maximum increase producible by boron. The chemical analyses for boron, whether "soluble" or "insoluble," do not correlate well with the quantity of boron nominally added to the liquid steel in the mold - a result that was to be expected.

4. In a given steel the increased hardenability correlates fairly well with the quantity of a "boron constituent" microscopically visible as a row of fine dots at the austenite grain boundaries when the steel is carefully heat-treated in a special way; despite many efforts to reveal it, this precipitate was not observed if the boron content by analysis was less than 0.0004 percent. When the boron by analysis is about 0.001 percent or higher, dots may appear as a band resembling a eutectic or eutectoid aggregate; when more than about 0.0035 percent boron is present, this constituent may appear after austenitizing at temperatures ordinarily used in practice and so may occasionally be evident in commercially heat-treated boron steel.

5. When a boron-treated steel is heated at a very high temperature for a very long time, the increase of hardenability due to boron gradually diminishes and finally disappears; nor is it restored by any subsequent heat treatment of such a "homogenized" steel. Moreover, under this treatment the characteristic "boron constituent" likewise gradually disappears, although boron content as measured by analysis remains unchanged. It is possible therefore that some part (or all) of the efficacy of boron in enhancing hardenability may be lost when the steel is heated for rolling or forging.

6. Addition of boron as Grainal to the 0.40- and 0.52-percent carbon series lowered the temperature at which austenite grains coarsened in a

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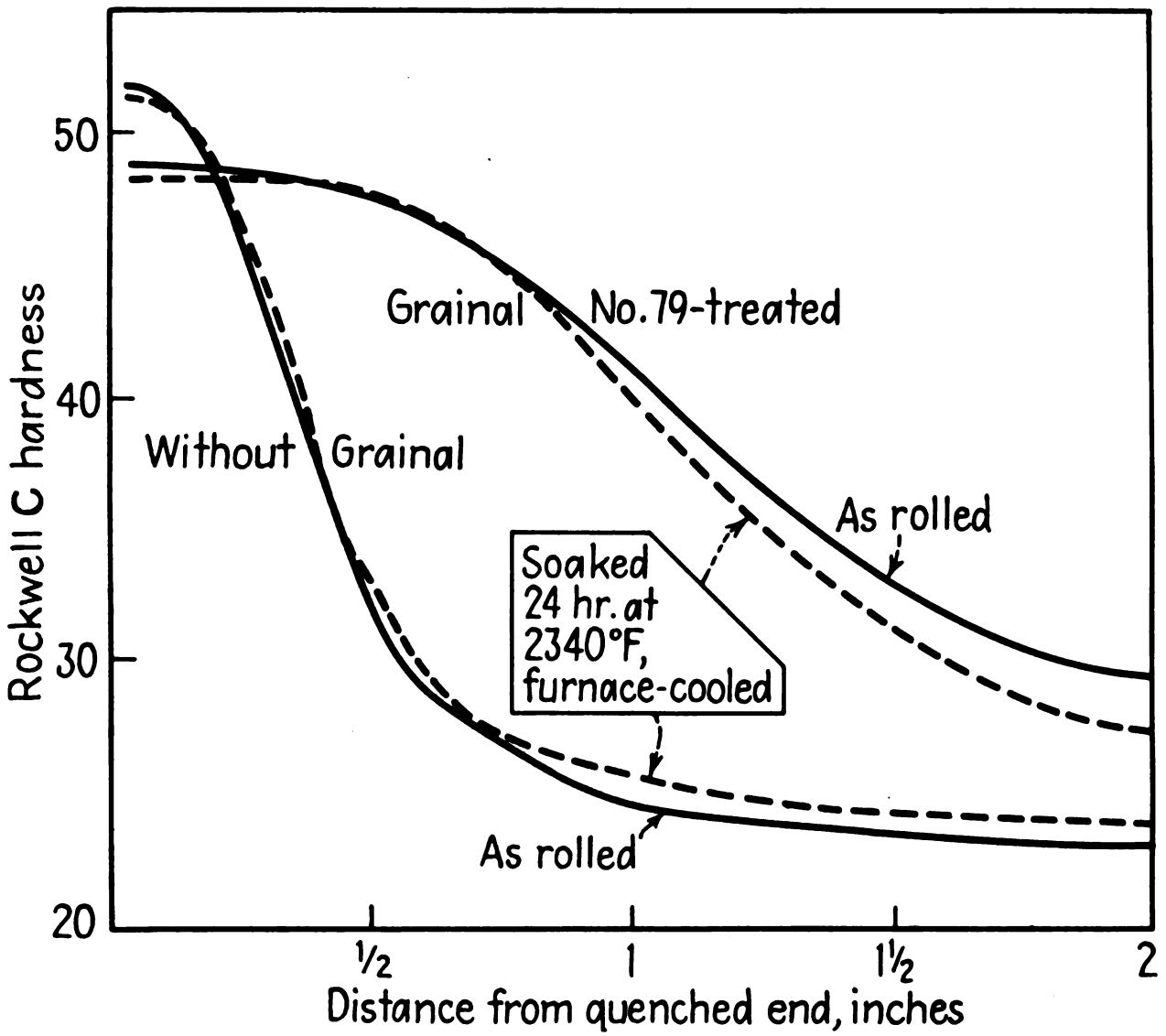

FIGURE 11.- Jominy test from center of billet of commercial T-1330 steel.

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given time. With increasing boron content the grain-growth behavior became more and more like that of steel which is not aluminum-killed, but this grain coarsening is only a minor factor in relation to the extra hardenability developed in the presence of a minute percentage of boron.

7. Certain modes of heat treatment develop in boron steels recognizable differences in microstructure as compared to comparable boron-free steel similarly treated. In the martensite-pearlite zone of end-quenched bars used for measuring hardenability, the austenite grains were outlined by pearlite in absence of boron, but not in boron steels. After austenitization about 1500° to 1600° F. (815° to 870° C.), as usually recommended, the presence of boron may increase greatly the number of undissolved particles.

Chandler and Bredig(132), in a discussion of the above paper, point out that in the case of commercial Grainal-treated steels handled in the usual manner with respect to soaking and forging temperatures, they have seen no examples in which the disappearance of the effect of the boron took place when the steel was heated. No significant change in hardenability was apparent in a Grainal 79-treated T-1330 steel, both before and after holding at 2340° F. for 24 hours, as shown in figure 11. The hardenability loss following high-temperature treatments was noted only in steels treated with ferroboron.

METHODS OF ADDING BORON TO STEEL AND RESULTS OF USING SPECIAL ADDITION AGENTS CONTAINING BORON

The art of adding boron to iron and steel has reached a high state of development.

Boron Addition Agents Used

Table 1 lists the composition of the boron-bearing addition agents used commercially. The alloys Silvaz, Silcaz, Bortam, Carbortam, Grainal, Grainal No. 1, and Grainal No. 6 (see table 1) are often referred to as "special deoxidizers" or "special addition agents," as they consist of various combinations of such elements as aluminum, boron, calcium, manganese, silicon, titanium, zirconium, and vanadium. The other boron alloys are principally binary combinations of boron with some other elements.

The boron-bearing addition agents may be divided into three groups:

1. Borax or other boron compounds.

2. Ferroboron, aluminum-boron, manganese-boron, or other metallic combinations.

3. The special addition agents or hardenability intensifiers.

It is not a generally recommended practice to use the first group, as results cannot be readily controlled.

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Concerning the second group, the Molybdenum Corp. of America reports that its type of ferroboron has a melting point which allows it to go into solution rapidly at liquid-steel temperatures. It is so made with a boron content that approximately 1/2 pound of the alloy per ton is added to obtain 0.003 maximum boron content. It is necessary to precede the addition of the ferroboron with all the deoxidizers and, in order to compensate for the grain-size coarsening effect of boron, they request that an additional 1/4 pound of aluminum per ton be added to take care of this feature.

The Electro Metallurgical Co. reports that thus far, nickel-boron has not been used commercially for the addition of boron to steel.

Concerning the third group, there is evidence for believing that the cumulative effect of all of the elements in such combination is desirable. Boron tends to coarsen grain size, and normally this tendency should be curved by association with grain-refining elements. The recent American Iron and Steel Institute report on Special Alloy Addition Agents(89) recommends that, in general, such agents should be added to the ladle; occasionally they may be put into the mold. A general summary of the report follows:

1. The use of special alloy addition agents will increase, with varying effect, the hardenability of all grades of steel studied, the degree depending on the base composition.

2. The most beneficial effect of the use of these agents on mechanical properties, especially ductility, is in steels heat-treated to high hardness levels.

3. To obtain the maximum results for any property, the steels to which these agents have been added must be quenched and tempered.

4. The base composition and section, as well as ultimate hardness, strength, or depth of hardening, are the major factors to be considered in determining those instances in which these agents can be used to maximum advantage.

5. The use of these agents will permit reduction in the quantity of strategic alloying elements previously used to give the desired tensile and impact properties in similar sections, thereby effecting savings in the alloy consumption for a given alloy-steel tonnage.

The Grainal Alloys

The Vanadium Corp. of America has made extensive reports on the results obtained by the use of these addition agents. The following is abstracted from these reports:

The effects produced by very small additions of the Grainal alloys, usually in the range of 2 to 6 pounds per ton of steel, are striking in

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that the changes in the properties of the steel are of a very high order of magnitude in respect to hardenability, ductility, toughness, and other required qualities. Fine-grained steels may be made deep hardening through the addition of Grainal alloys.

These alloys contribute to quenched and tempered steels (especially at high hardness), tensile ductility (elongation and more particularly reduction of area), and also impact strength far above the values obtainable in ordinary steels to which they have not been added.

The Grainal alloys also contribute significant improvement to steel parts that are subject to surface-hardening treatments such as carburizing, cyaniding, nitriding, quenching of heated surfaces, and the like.

The singular effects of the Grainal alloys have been applied in carbon steels and low-alloy steels for constructional purposes; improvement is also imparted to higher-alloy steels and to higher-carbon steels.

The addition of Grainal to low- and high-manganese, 3.5 percent nickel steels increases the hardenability as determined by General Motors tests 4 and 2 fold, respectively, and increases the depth of hardening to Rc 50 of 0.40-percent carbon and 0.59-percent carbon-silicon-molybdenum steels 2.4 and 2.2 fold, respectively.

Low-manganese steels

C	Mn	Si	Ni	Treatment	Rc50, in.	Rc40, in.
0.32	0.38	0.20	3.60	-	1/8	5/16
.34	.37	.20	3.54	grainal	1/2	1

High-manganese steels

0.38	0.80	0.16	3.57	-	5/16	1/2
.36	.78	.15	3.58	grainal	5/8	2

Effect of Vanadium Grainal No. 1 Treatment of Steel Made to Specifications S.A.E. 1040

The test bars in the following series were heat-treated as follows:

Samples for 450° F. draw:
1,650° F. normalize.
Preliminary machine to 0.55 inch.
Quench from indicated temperature.
450° F. temper.

Samples for 900° F. draw:
1,650° F. normalize (1-inch round),
Quench from indicated temperature.
900° F. temper.
Machine.

Chemical analysis

	C	Mn	Si	S	P	V	A.S.T.M. grain size
Basic O.H., S.A.E. 1040	0.40	0.75	0.22	0.028	0.011	None	6, few 4
Basic O.H., S.A.E. 1040	.40	.75	.21	.028	.013	.046	5-6, few 4

4 lb. Vanadium Grainal No. 1 per ton.

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Oil quench

Temper, °F.	Quench, °F.	Type	Yield point	Tensile strength	Elong.	R.A.	B.H.N.	Izod	"P" value[1]
450	1,525	S.A.E. 1040	88,150	121,750	20.5	58.8	229	85.5	95
		S.A.E. 10T40-Grainal	231,250	266,000	12.0	46.9	510	20.5	109
900	1,550	S.A.E. 1040	75,300	107,400	22.0	59.8	217	75.5	93
		S.A.E. 10T40-Grainal	144,850	155,600	16.0	60.3	325	60.8	104

Water quench

Temper, °F.	Quench, °F.	Type	Yield point	Tensile strength	Elong.	B.A.	B.H.N.	Izod	"P" value[1]
450	1500	S.A.E. 1040	184,350	215,800	5.0	24.4	477	12.0	72
		S.A.E. 10T40-Grainal	219,250	262,200	10.5	50.9	495	-	113
900	1525	S.A.E. 1040	87,400	116,000	21.0	61.6	237	83.0	97
		S.A.E. 10T40-Grainal	140,750	150,350	16.0	60.3	313	64.0	102

1/ The "P" value is calculated from the formula: $P = \frac{TS + 6000\ RA}{5000}$ and serves as a toughness-strength factor.

Similar results are obtained for steel made to specifications 1045, 1050, and 1055.

Effect of Grainal Treatment of Steel Made to Specifications N. E. 9422

Hardenability Tests. - The marked effect of the Grainal addition in increasing the capacity for hardening of this base steel composition is quite apparent from the Jominy curves. While both steels actually come up to a Rockwell "C" hardness of 50 on the end of Jominy specimen, this value was not attained along the side; therefore, for these low carbon steels, comparison is drawn customarily on the basis of a Rockwell "C" hardness of 40, which was obtained 0.15 inch from the quenched end of the specimen for the untreated steel, while 0.63 inch is the corresponding position in the Grainal-treated steel.

Tensile and Izod Tests. - The effect of the Grainal treatment on the tensile and Izod impact properties of the two steels is shown for various heat treatments by the following data. At 0.25 percent carbon, the chemistry of the steels is on the hard side for some carburizing applications.

It should be observed in the case of steel of this particular composition that a contribution by Grainal to hardenability is such that there is obtained in a comparison of oil-quenched small bars a simultaneous increase in those properties representing useful strength and those representing ductility and toughness. In the case of water quenching, the strength properties alter little at the low tempering temperatures, but ductility and toughness are simultaneously increased when this quenching medium is used. With increased tempering

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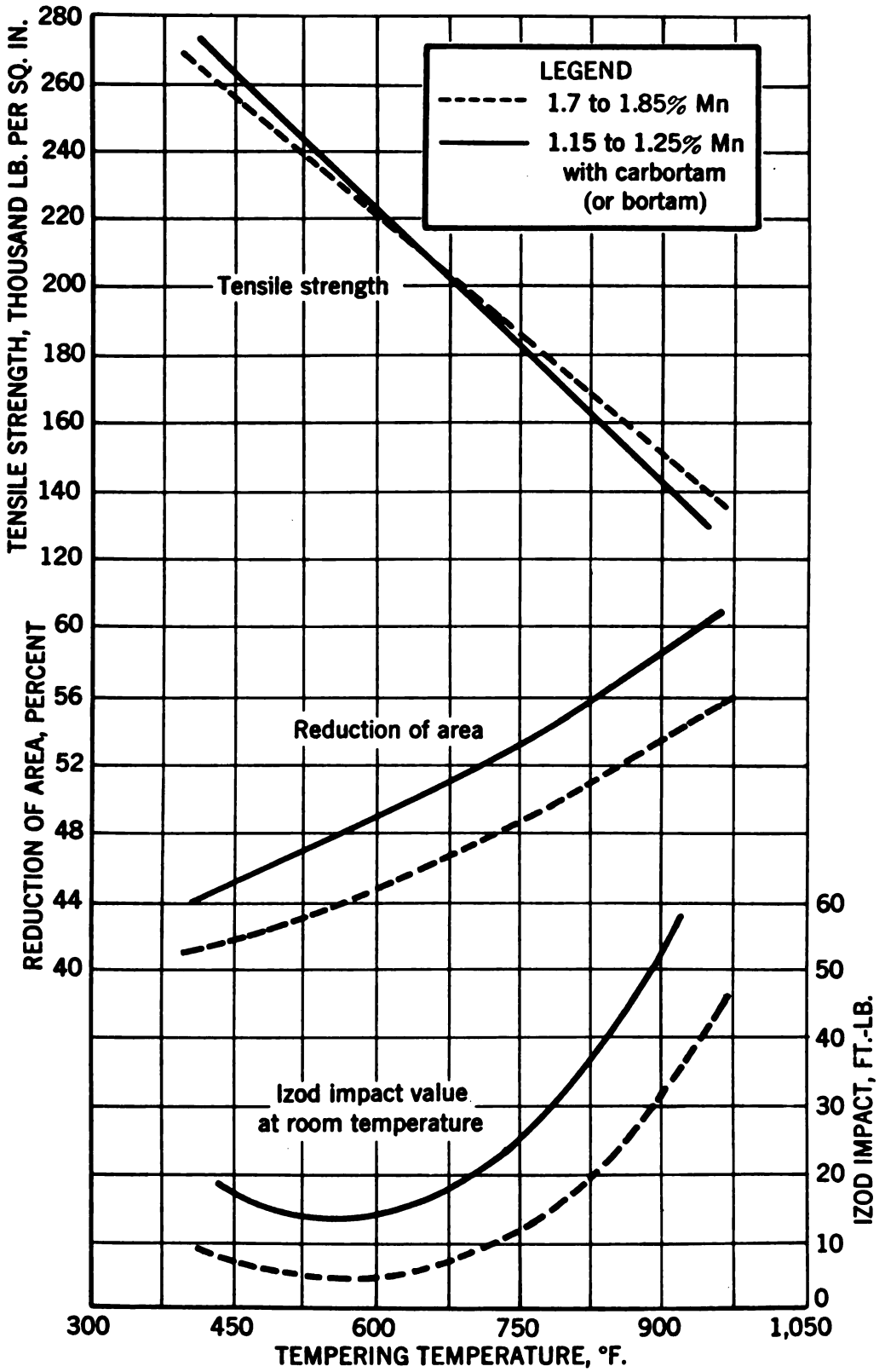

FIGURE 12.- Variation of some properties of quenched manganese and Carbortam-treated 0.37- to 0.40-percent carbon steels, respectively, with different tempering temperatures.

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temperature, the rate of fall of hardness is less than in the untreated steel, thus affording over a very wide range of heat treatment a substantial improvement in all properties involved in considerations of utility.

Tabulated below are the surface hardnesses (Brinell 3,000 kg.) on 1-inch rounds, either oil- or water-quenched, from various temperatures:

Oil		Quenching temperature, °F.	Water	
N.E. 9422	N.E. 94T22 Grainal		N.E. 9422	N.E. 94T22 Grainal
179	207	1300	212	209
302	300	1400	363	363
311	311	1425	388	383
302	331	1450	415	415
302	420	1500	477	461
282	415	1550	477	477
311	417	1600	477	477
306	415	1650	461	477
277	415	1700	477	461
307	415	1750	477	461
321	409	1800	477	448
311	409	1900	461	461

For the as-quenched condition, the Grainal-treated steel shows definitely more effective hardening in oil than the base steel, thus confirming the other physical test results. Water quenching brings both steels into the same hardness classification, but reference to the other physical property values still shows the Grainal steel to have superior qualities after treatment in both quenching mediums.

Similar results are obtained with steel made to Specifications N.E. 9440. These results are available in trade publications of the Vanadium Corp. of America.

The Alloys Bortam and Carbortam

The melting point of Bortam is approximately 2,350° F.

The melting point of Carbortam is approximately 2,650° F.

The results of Comstock's(99) work with these alloys may be conveniently summarized by the curves of figure 12.

It is evident from these results that if pearlitic manganese steel of about 140,000 to 260,000 lbs. per sq. in. tensile strength in the quenched and tempered condition is required, the steel will have better ductility and resistance to impact if the strength is obtained by treatment of a steel containing about 1.15 to 1.25 per cent manganese with Bortam or Carbortam, than if a steel with about 1.8 per cent manganese is used, without any boron addition. Both kinds of steel have practically the same hardenability, and the boron alloy treatment, if Carbortam is used, is even more

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economical than the extra manganese required for hardenability and strength without it. The rapidly increasing popularity of these titanium-boron alloys is thus logically accounted for by the advantages illustrated by the test results here reported.

Comstock(116) studied the effect of boron in N. E. 9440 and S. A. E. 4640 steel. The following is a summary of his results:

Summarizing the results that have been reported it appears that satisfactory hardenability is secured in NE 9440 steel without either chromium, or nickel and molybdenum (except for residuals obtained from scrap) if Carbortam treatment is used. In the SAE 4640 steel, the Carbortam treatment gives even better hardenability than 1.2 percent nickel or 0.25 percent molybdenum, but when molybdenum is saved in this way it should be remembered that the hardness at slower cooling rates is lower, and lower tempering temperatures are required for equal strength.

The tensile tests of oil quenched and tempered specimens showed but little difference between the regular NE9440 steel, and the steels with Carbortam treatment substituted for the chromium, or for the nickel and molybdenum. These Carbortam-treated steels had a slight advantage in impact resistance, though not in hardness as oil-quenched and tempered. In the SAE 4640 steel there was no appreciable difference in tensile or impact properties of the quenched and tempered specimens when the Carbortam treatment was used in place of about 1.2 percent nickel. When Carbortam was used instead of about 0.25 percent molybdenum, however, the strength was lower and the ductility and impact values higher, at the same tempering temperatures. These differences are easily corrected as has been noted, by using a slightly lower tempering temperature for the Carbortam treated nonmolybdenum steel.

In machinability no significant differences between the similarly heat-treated steels, other than those to be expected from slight variations in hardness, were brought out by the tests.

The results of this investigation thus indicate that practically equal tensile properties, and at least as good, or in some instances even better, notched-bar impact resistance, are obtained in the quenched and tempered condition when treatment with Carbortam is substituted for chromium, molybdenum or nickel in NE 9440 or SAE 4640 steel. The hardenability and machinability of the steels are also not inpaired by this substitution. The omission of molybdenum, however, may necessitate the use of slightly lower tempering temperatures for equal properties.

It is important that the correct amounts of other alloys are omitted when Carbortam is used, for it will not replace successfully unlimited amounts of other hardening agents, and if too much

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of the other hardening agents is present with the boron, excessive hardenability will result. This work indicates that enough Carbortam added to give 0.003 to 0.004 percent boron in these laboratory melts successfully replaces about 0.6 percent chromium, 1.2 percent nickel, or 0.25 percent molybdenum. This equivalent amount of chromium is higher than has previously been suggested, but those for nickel and molybdenum are in agreement with previous recommendations.

Borosil

The Ohio Ferro Alloys Corp. reports that Borosil has proved an excellent form of addition agent, giving uniform distribution of boron and uniform recovery from heat to heat. The boron content is reported to affect hardenability to a greater extent than any alloying element except carbon. The company also recommends the use of Borosil as a deoxidizer, with a wide application in the formation and distribution of inclusions to produce more uniform steels. This alloy has a relatively low melting point, and this, together with the low boron content, aids in a uniform recovery of the boron in the finished product.

Charts are given in the American Iron and Steel Institute report(89) comparing the hardness of treated and untreated steels, and the evidence in favor of the addition-agent treatment is conclusive.

DETERMINATION OF BORON IN IRON AND STEEL

General Considerations

In any method for the determination of boron, it should be remembered that solutions containing free boric acid should never be boiled in open vessels, for the acid is very volatile with steam. The loss of boron as the trifluoride or the introduction of boron into the solution by the attack of borosilicate glassware (pyrex) by alkalies should be guarded against in analyses of the highest accuracy. Boron-free glassware suitable for use in analytical work involving boron can be obtained from the Corning Glass Works, Corning, N. Y.

To get rid of boron, the acid solution is usually evaporated to dryness, the residue treated with 25 ml. of absolute methyl alcohol or methyl

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alcohol saturated with hydrochloric acid gas, and the solution again carefully evaporated to dryness after covering with a watch glass. Four or five treatments are usually required. Boron can also be volatilized and completely removed from solutions in which it is not wanted by evaporating to dryness with hydrofluoric acid, or to fumes with a mixture of sulfuric and hydrofluoric acids.

Early Methods Reported in the literature

Chapin's method(1) depends upon the solution of 1 gram of steel in dilute hydrochloric acid under a reflux condenser, oxidizing with hydrogen peroxide, and volatilizing the boron with methyl alcohol by several distillations. After the alcohol in the distillate is evaporated, the solution is titrated with standard sodium hydroxide. This method is subject to an error of 0.03 percent.

Lindgren's method(7) calls for dissolving 3 grams of steel in equal portions of nitric and hydrochloric acid (20 ml. in all) and neutralizing with calcium carbonate (usually about 30 grams of $CaCO_3$). After all carbon dioxide is boiled off, the precipitate is filtered, and the boron in the filtrate is titrated with standard sodium hydroxide.

Chapin's method is long and tedious, and the accurate determination of a very small amount of boron when using a 1-gram sample is improbable, as the method is subject to a 0.03-percent error. Lindgren's method is open to the objection that a small amount of boron in the large mass of precipitate made by 3 grams of iron and 30 grams of $CaCO_3$ presents a difficult analytical problem.

The final estimation of boron by sodium hydroxide titration, as suggested in these methods, does not yield consistent results, as the blank is occasionally equivalent to 10 times the boron content. The blank is due to carbon dioxide, which may be present in the water and especially in the sodium hydroxide.

Methods Available

Four methods (A,B,C, and D) determining boron in iron and steel are described by Lundell, Hoffman, and Bright(10). Method A depends upon the volatility of methyl borate, $B(OCH_3)_3$, which boric acid forms with methyl alcohol. The method consists in volatilizing the ester, $B(OCH_3)_3$, saponifying it in alkaline solution to obtain Na_3BO_3, expelling the alcohol, titrating so that boric acid, H_3BO_3, is the only acid present, and then resuming the titration under conditions that give the compound NaH_2BO_3. The reaction can be illustrated by the equation.

$$H_3BO_3 + NaOH \longrightarrow NaH_2BO_3 + H_2O.$$

A. Distillation of Methyl Borate and Titration

Special solutions required. Paranitrophenol. - Dissolve 1 gram of the reagent in 75 ml. of neutral ethyl alcohol, and dilute to 100 ml. with H_2O.

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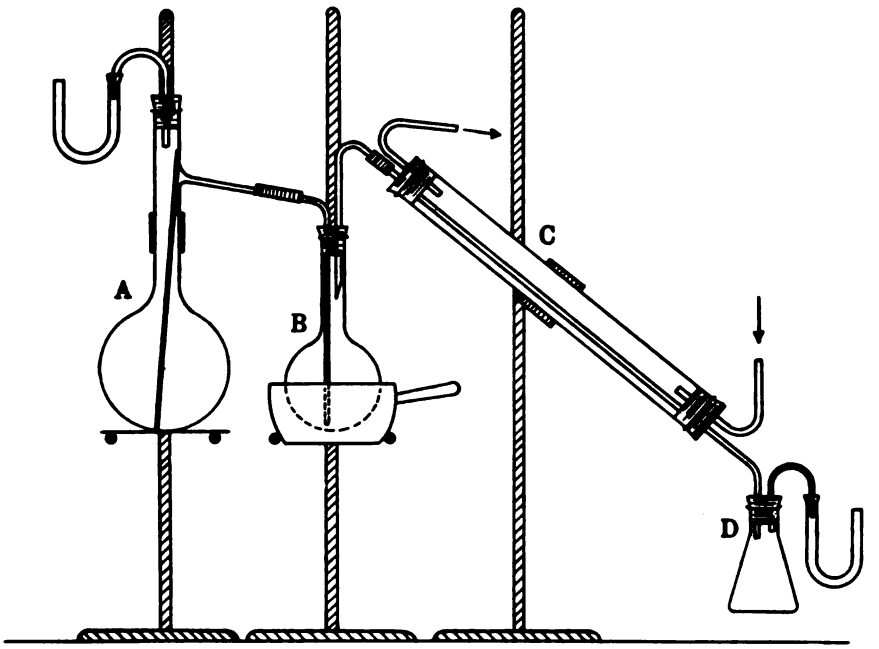

FIGURE 13.- Distilling apparatus for boron.

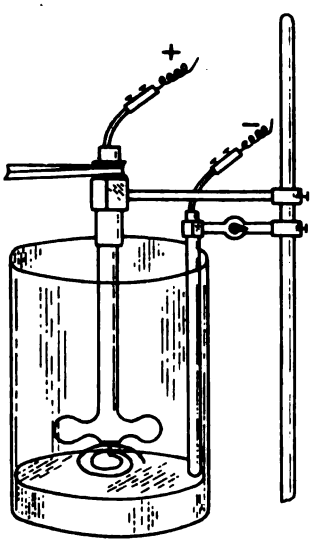

FIGURE 14.- Mercury cathode cell.

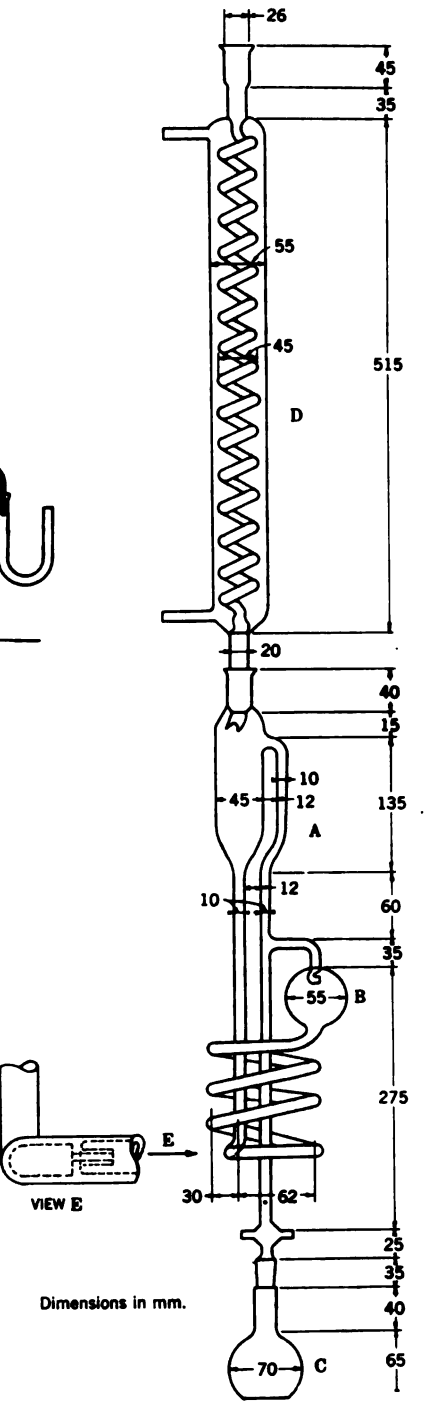

FIGURE 15.- Partheil distillation apparatus used for determining boron.

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Phenolphthalein. - Dissolve 1 gram of the reagent in 100 ml. of neutral ethyl alcohol, and dilute to 200 ml. with H_2O.

Hydrochloric acid 0.1 N. - This need only be approximate and should be prepared so that it is free from CO_2.

Sodium hydroxide, 0.5 N and 0.1 N. - These solutions should be free from CO_2. The former is used in preliminary titrations, and the exact strength need not be known. The 0.1 N solution is standardized as follows: Fuse pure boric acid in a platinum dish. While still warm, crush the melt, and place the pieces quickly in a weighing tube. Dissolve 1.741 grams in 250 ml. of warm, recently boiled H_2O, cool, and dilute the solution to 500 ml. This solution can be regarded as exactly 0.1 N (1 ml. represents 0.00108 gram of boron). Standardize the 0.1 N solution of NaOH against suitable portions of this solution by titrating as described in the method, preferably after the solution has been carried in company with 1 gram of boron-free iron through all steps of the method that is to be used.

Methyl alcohol. - A good grade of methyl alcohol should be distilled over lime after it has been heated for some hours in contact with the lime under a reflux condenser. The more nearly anhydrous the alcohol the better; and volatile organic acids must, of course, be absent.

Calcium chloride. - This should be granular, anhydrous, and free from boron.

Mannite. - The ordinary reagent.

Special apparatus required. - See figure 13.

Procedure. - Prepare 10 to 25 ml. of solution containing no more than 0.5 ml. of HCl in excess and no volatile organic acid.5/ Transfer to flask B (fig. 13); and, through a paper funnel to keep the neck of the flask clean, add 1 gram of pure anhydrous $CaCl_2$ for each milliliter of solution. Twirl the flask a little to allow the chloride to take up the water. Connect the flask with the rest of the apparatus, and raise the casserole beneath it until the flask rests in the water, but does not touch the bottom. Begin the distillation of alcohol from A, taking care that the open end of the capillary "boiling tube" is free from alcohol and that the U-tube attached to the receiver is trapped with water. Do not heat decomposition flask B until about 25 ml. of alcohol has condensed in it. After that, heat the water bath by a small flame, and thus keep it hot enough to prevent further condensation of alcohol in the flask. At no time should distillation be so rapid as to permit escape of methyl borate from the system. When 100 ml. of distillate has collected in receiver D, exchange the flask for a new one, and keep on gathering distillate. Add the contents of the trap tube to the first receiver, and run a preliminary titration as follows: Add 1 drop of paranitrophenol solution (no more), and

5/ In the case of irons or steels, it would seem that 1 gram of sample might be dissolved in 15 ml. of dilute HCl(1:2) under a reflux condenser, oxidized by boiling for a few minutes with 1 ml. of H_2O_2 (30 percent), cooled, and then transferred to flask B with a minimum of H_2O and without wetting its neck or sides.

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then run in the standard 0.1 N NaOH until the indicator shows that the free mineral acid is neutralized. Next, add 1 ml. of the phenolphthalein solution, and continue the titration until the color of the indicator begins to appear. The end point will not be sharp, but the amount of alkali used between the two end points indicates approximately the amount of boric acid in the distillate. After the titration is completed, add twice as much alkali as was used between the two end points. Transfer the distillate to the second distilling apparatus, and boil off the alcohol.

In the meantime, the second 100 ml. of distillate will have collected. This should contain the remainder of the boron if the alcohol was anhydrous and enough calcium chloride was used. Stop the distillation, and remove the receiver. Treat the second distillate exactly like the first, and add it to the first. As a rule, no more than 1 ml. of 0.1 N NaOH will be required.

When the liquid from which the alcohol is being distilled no longer boils in the steam bath, remove it to a casserole, and rinse the flask once or twice with water. Heat the casserole over a free flame, rotating while doing so, until the little remaining alcohol has been boiled out. The volume of solution should now be small - usually less than 25 ml. Adjust to 25 ml., return the solution to the flask, and add dilute HCl (1:1) drop by drop with constant stirring, until the color of both indicators is discharged, taking care not to add a drop too much. Now put in the "boiling tube," heat the flask on the steam bath for a minute or two, then attach to the filter pump, and distill under reduced pressure until the liquid is nearly cold and only an occasional bubble appears. Break the vacuum, cool if necessary under the tap, and proceed with the final titration as follows:

First neutralize the excess of hydrochloric acid by carefully running in 0.5 N NaOH until the yellow of paranitrophenol just appears. Bring back to acid reaction with the 0.1 N HCl and then to the appearance of a faint yellow with 0.1 N NaOH. This end point must be reached exactly, for all HCl must be neutralized. and all of the H_3BO_3 must be left. One drop of 0.1 N HCl should discharge the color, and 1 drop of 0.1 N NaOH should bring it back.

Now add 1 gram of mannito,[6/] read the 0.1 N NaOH burette, and continue titrating to the end point for phenolphthalein. Add another gram of mannito. If this causes the color to disappear, resume the titration with alkali, and so continue until the color remains after the mannite has been added.

Correct the volume of 0.1 N NaOH required by the volume required in a blank run, preferably carried through all steps of the method, and multiply by the boron titer of the solution.

The changes of color that take place during the titration need mention. When the mannite is added to the solution, the yellow color due to the

6/ Glycerin can be used instead.

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paranitrophenol disappears at once if boric acid is present. This is due to the fact that mannite (as well as glycerin) forms a complex with the compound NaH_2BO_3, involving the elimination of 2 molecules of water. As titration proceeds, the color reappears and grows stronger, becoming less intense just before the phenolphthalein end point appears. The latter will be noticed as a faint brownish tinge, and then another drop of the 0.1 N alkali changes it to an intense brownish red, which is the real end point.7/

Method B for the determination of boron in iron depends on the separation of boron with calcium carbonate.

B. Precipitation with Calcium Carbonate and Titration

Procedure. - Transfer 2 to 3 grams of iron to a round-bottomed 800-ml. Jena flask, and treat with a mixture consisting of 10 ml. each of HNO_3, HCl, and H_2O. When reaction is complete, cool to room temperature, agitate vigorously, and add at one stroke double the amount of dry, finely powdered $CaCO_3$ needed for complete neutralization. Add 250 to 300 ml. of CO_2-free water, and boil the solution under a reflux condenser for at least 30 minutes to break down bicarbonates and to expel CO_2. Add about 30 ml. in bulk of well-washed asbestos fiber suspended in hot water, and boil for 3 to 5 minutes. Filter at once by suction through a Buchner funnel about 15 cm. in diameter and having a double thickness of filter paper carefully fitted over the bottom. A splash-trap should be connected to the receiving flask. Wash the precipitate 8 to 10 times with boiling hot H_2O, remove the funnel, and insert a rubber stopper. Renew the suction to cause further boiling and expulsion of CO_2.

Cool, and add a few drops of phenolphthalein and then a 0.1 N solution of NaOH (free from carbonate), until a pink color appears. Add 1 gram of mannite, and continue the titration until a permanent pink color is obtained. Add another gram of mannite, and again titrate if the color disappears. Subtract the volume of 0.1 N solution required in a run in which boron-free iron is carried through all steps of the process, and multiply the corrected volume by the boron titer of the solution.

For standardization of the 0.1 N NaOH see the preceding method (A).

Method (C) depends on the separation of boron by electrolysis over a mercury cathode. The steel is dissolved in dilute H_2SO_4 under a condenser and oxidized with H_2O_2, all the Cr, Ni, Cu, Fe, and the like are removed by electrolysis with a mercury cathode, and the boron is determined

7/ Other indicators can be substituted provided the color change occurs at approximately the same pH as does that of the indicator which is replaced and is not seriously affected by methyl alcohol. Thus some prefer methyl orange to paranitrophenol, and some prefer p-α-naphtholphthalein (yellow at pH 7, blue at pH 9) to phenolphthalein. With the naphtholphthalein the end point would be green (yellow of methyl orange or paranitrophenol plus blue).

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by titration as usual in the electrolyte. This is Tschischewski's method.(9) It is believed this method does not function satisfactorily because of the presence of sulfate ions in the solution.

C. Electrolysis with a Mercury Cathode and Titration

Procedure. - Treat 0.5 to 1 gram of the alloy with 10 to 15 ml. of dilute H_2SO_4 (1:3), and heat under a reflux condenser until solution is complete. Cool somewhat, add 3 to 5 drops of H_2O_2 (30 percent), and again boil for a few minutes. Add 50 ml. of cold H_2O and then N NaOH (free from CO_2) until the H_2SO_4 has been neutralized. Next add 3 to 5 drops of H_2SO_4, and electrolyze at 5 amperes and 10 to 15 volts with a mercury cathode. The temperature of the electrolyte should be kept below 30° C. For this reason, the cell shown in figure 14 is desirable. This is 6.5 cm. wide and 11 cm. high, and mercury is poured to a height of 2.5 to 3 cm. Connections are made as shown, the stirrer is revolved at 350 r.p.m., and the cell is cooled in cold water. When electrolysis is complete (about 30 minutes), draw off the liquid as the current is still passing, and rinse the vessel and mercury. If the solution contains more than 15 mg. of boron, it should be diluted to exact volume and a suitable aliquot portion taken. Transfer the solution (not over 100 ml. in volume) to an Erlenmeyer flask, add 3 to 5 drops of methyl orange, and then titrate with a 0.05 N solution of NaOH (free from CO_2) until the color is faint rose. Continue the titration (with 0.01 N NaOH if the amount of boron is very low) until the color just changes to orange, as determined by comparing with a previously prepared standard. If desired, the end point can be fixed by adding an excess of the alkali and then carefully adding 0.05 or 0.01 N H_2SO_4. All the boron should now be present as boric acid. Add a few drops of phenolphthalein, take the reading of the alkaline solution, and then add it dropwise until the solution begins to show pink. Add 1 gram of mannite, and again titrate to a faint pink color. Add another gram of mannite, and so continue as long as the addition of the mannite causes the color to disappear. When a permanent end point is obtained, again take the reading.

One milliliter of 0.01 N alkali represents 0.000108 gram of boron. If an 0.05 N solution is used it represents five times as much. The strength of the solution should be checked by titration against pure fused B_2O_3 which has been carried through all operations in company with a suitable portion of steel that is free from boron.

Glycerin can be used instead of mannite. In this case the glycerin must be carefully neutralized before use. Approximately 10 ml. is needed, and the end point taken is that which is not affected by the addition of 5 ml. more of glycerin.

Method D depends on the extraction of boron by long boiling with ether and its precipitation and weighing as boron phosphate, BPO_4.

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D. Weighing as Boron Phosphate

Dissolve 1.2 grams of steel in a mixture of 10 ml. of HCl and 5 ml. of H_2O under a reflux condenser. Oxidize with 15 to 20 ml. of H_2O_2 (3 percent), and boil for 10 minutes. Cool and pour into a 300-ml. measuring flask. Precipitate the iron, chromium, and the like by adding 30 ml. of a solution of pure NaOH (1:3). Dilute to the mark, mix, and filter to obtain exactly 250 ml. (representing 1 gram of sample). Transfer to a platinum dish, and evaporate to about 10 ml. Cool in ice water, and add dilute HCl (1:1) until acid. Transfer to tube A (fig. 15), and wash with as little water as possible. Next carefully add enough freshly rectified ether so that the bulb B is nearly full. Add 20 ml. of ether to the flask C, and connect C, B, and D. The acidified solution of the borate must not rise in B more than one-third of the way, and none of the solution must enter D or the tube leading from B to C. Warm C on an electrically heated water bath to a temperature at which the ether boils briskly and the condensed ether flows into A in a steady stream. Extract thus for 19 to 20 hours. Cool, draw off the ether into flask C, and pour into a weighed platinum dish. Treat with 1 gram (with small amounts of boron, 0.3 gram) of $(NH_4)_2HPO_4$, evaporate to dryness, and heat to constant weight over a Bunsen burner. Weigh as BPO_4.

The following two methods are described by the U. S. Steel Corp.(14) Method E is a combination of methods B and C, designed to permit the determination, most conveniently, of boron in the presence of other common alloying elements.

E. Electrolysis Over a Mercury Cathode and Calcium Carbonate Separations

Special Solutions Required. - All solutions must be prepared and kept so that they will be free of CO_2.

Phenolphthalein Indicator Solution - Dissolve 1 gram of phenolphthalein in 100 ml. of neutral ethyl alcohol freshly distilled from CaO and add 100 ml. of CO_2-free water.

Mannite - Use solid reagent. This compound, correctly designated as mannitol, has the formula $C_6H_8(OH)_6$.

Standard sodium hydroxide solution, 0.1N - Dissolve 100 grams of NaOH in 100 ml. of H_2O in a waxed tube. Since the solution must be absolutely free of carbonate, add a few ml. of $Ba(OH)_2$, and let the solution stand several days tightly stoppered or closed with a stopper bearing a CO_2 trap. Carefully draw off 6.5 ml. with a calibrated pipette, and dilute to 1 liter with freshly boiled cold water. To standardize the solution, use pure boric acid as follows: Fuse the acid in platinum dish, crush while still warm, and weigh 1.741 grams in a weighing bottle. Add to 250 ml. of warm, freshly boiled water. Cool and dilute to 500 ml. for a 0.1N solution and to 1 liter for a 0.05N solution. One ml of 0.1N solution equals 0.00108 gram of boron. Standardize the NaOH solution against this solution by direct titration, using the same volumes, etc., as directed in the method. Also add measured amounts to a boron-free steel solution and analyze by the same procedure used in analyzing the sample.

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Solution of the Sample and Separation by Electrolysis. - Transfer 1 gram of the sample of steel to a 150-ml. Erlenmeyer flask equipped with a reflux condenser. Ad 15 ml. of dilute sulfuric acid (1:4), and let the steel dissolve in the cold, if it will. If not, heat gently until solution is complete. Cool, if necessary, add 5 to 8 drops of 30-percent H_2O_2 (Perhydrol), and boil for several minutes to oxidize the iron, etc. Pour 50 ml. of warm water through the condenser to rinse it, disconnect it, and rinse the wall of the flask with a fine jet of water. Neutralize with 1 N NaOH solution, CO_2-free, and acidify with 0.2 ml. of H_2SO_4 (sp. gr., 1.84). Transfer to a 250-ml. beaker containing about 1 inch of pure mercury, set the beaker in cold water, and electrolyze at 5 amperes and 10 volts until the solution is practically free of iron, keeping the temperature below 30° C. with ice water, if necessary. During the electrolysis, stir the solution mechanically, if possible; otherwise, keep it agitated by stirring frequently by hand. Decant the solution from the mercury into a small beaker and treat as directed below.

Titration of H_3BO_3; Absence of Al, As, Cb, Ta, Ti, W, V, or Zr. - Filter the solution into a 250-ml. beaker, and wash with water to a total volume of 100 ml. Add 3 to 5 drops of methyl orange, and titrate the free H_2SO_4 with 0.05 N NaOH to a faint rose color, then dropwise (preferably with 0.01 N solution if boron is low) to orange. Back-titrate with 0.05N H_2SO_4, if desired to fix the end point. Add a few drops of phenolphthalein, take the alkaline reading, and continue adding the sodium hydroxide solution until the solution begins to show pink. Add 1 gram of mannite, and titrate to a faint pink. Repeat until the addition of mannite does not cause the color to disappear, and take a reading. Calculate the percentage of boron in the sample.

Separation with $CaCO_3$ and Titration of H_3BO_3. - Transfer the electrolyzed solution to a round-bottom 600-ml., Jena flask equipped with a reflux condenser; add 1 gram of ferric sulfate or chloride and 100 ml. of water. Mix and add, all at once, twice as much very finely ground pure calcium carbonate as is required to neutralize the acid, and boil the solution under the reflux condenser for 30 minutes to decompose bicarbonates and expel CO_2. Add 50 ml. of well-washed asbestos fiber suspended in hot water, and boil 5 minutes longer. Filter through paper in a Buchner funnel, and wash 8 to 10 times with boiling water. Remove the funnel, and apply the suction direct to the flask to cause low-temperature boiling and expel CO_2 completely.

Cool the solution rapidly to room temperature, add a few drops of phenolphthalein solution, and titrate with 0.05 N NaOH to a pink color. Add 1 gram of mannite, and add more NaOH to a pink end point. Repeat the addition of mannite and the titration until mannite does not cause the pink color to fade. Subtract the milliliters of NaOH used in the blank run, using the same amount of ferric sulfate or chloride, and multiply the corrected volume by the boron titer of the NaOH solution. Multiply by 100, and divide by the weight of sample used to find the percentage of boron.

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The U. S. Steel Corp.(14) states that the following method gives reasonably accurate results for the determination of boron in iron and steel.

F. Method Based Upon the Calcium Carbonate Separation

Transfer 2 to 3 grams of the sample and the same weight of a sample of steel free of boron but otherwise of similar composition to separate round-bottom flasks, and treat each with a mixture composed of 10 ml. of H_2O, 10 ml. of HCl, and 10 ml. of HNO_3, using no more than is necessary to dissolve the sample and leave a moderate excess. When action of the acid mixture has ceased, cool the flask and contents to room temperature, rinse the neck with a little water, and, while agitating vigorously, add dry, finely powdered calcium carbonate ($CaCO_3$) to complete neutralization of the solution. To decompose bicarbonates formed and expel carbon dioxide, add 250 ml. of freshly boiled water, attach the flask to a reflux condenser, and boil the mixture for 30 minutes or longer. Introduce about 50 ml. of a hot, neutral, water suspension of thoroughly washed asbestos fiber, and continue the boiling for 5 minutes.

Filter the mixture by suction upon a Büchner funnel, and wash the insoluble matter 10 times with boiling hot water. Remove the funnel, and apply suction direct to the flask to free the solution entirely of CO_2. Cool rapidly to room temperature, and proceed with the titration at once.

Titrate both the blank and the sample with 0.1 N NaOH and mannite, as directed in the last paragraph of the preceding method. From the volume of the 0.1 N NaOH solution required to titrate the sample, subtract the number of milliliters required to titrate the blank. Multiply the difference by the boron titer of the solution, and by 100, and divide by the weight of sample used to find the percent boron in the sample.

A1. The Distillation - Titration Method

As the result of modifications of method A by Hague and Bright,(13) distillation as methyl borate followed by alkalimetric titration has become a reliable process.

Hague and Bright(13) described a method for determining small amounts of boron in steels and irons. The procedure calls for (1) solution of the sample in hydrochloric acid followed by oxidation with hydrogen peroxide, (2) distillation of methyl borate (Chapin's method), and (3) titration of boric acid with sodium hydroxide in the presence of mannite. Selenium and tellurium do not interfere; but germanium, a very minor constituent rarely present in ferrous alloys, causes small positive errors. Hague and Bright give directions for examining any acid-insoluble material for boron. Data obtained by applying the method to a number of ferrous alloys show that results accurate to $\pm$0.002 percent can be expected with irons and steels containing 0.005 to 0.1 percent of boron.

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Concerning this method, Sayre(24) reported it can be used successfully in determining quantities varying from 0.0001 to 0.005 percent of boron. Under general continuous laboratory practice, steels containing small quantities of boron can be analyzed to ±0.0003 percent boron. Some work has indicated that the amount of borax present in the laboratory glassware as borates may have an effect on the end result. The chief disadvantage of this method is the long procedure required. Hague(24) described a new technique for determining the boron content of the residual matter left as a byproduct of the distillation-titration process. Results show that in most cases the quantity of boron remaining in insoluble compounds is actually larger than the dissolved boron. In virtually every case, the end analysis of standard samples shows that this method gives less than actual content.

Kar(15) applied the quinalizarin and curcumin tests to the determination of boron in steel.

G. Colorimetric Method Using Quinalizarin

Procedure. - The quinalizarin reagent used in this test is prepared simply by adding 5 mg. of quinalizarin to 100 ml. of concentrated sulfuric acid and stirring. The actual procedure used in determining boron in steel is as follows:

Transfer 1 gram of the steel to be analyzed to a 500-ml. flask, and add 15 ml. of 1:5 sulfuric acid. Heat on an electric plate under a reflux condenser until the action is complete. Oxidize with 2 ml. of 3 percent hydrogen peroxide poured through the condenser, and boil for 15 minutes. Cool, filter, and electrolyze by a mercury cathode to separate the iron, manganese, chromium, etc. Filter the acid solution, add 10 ml. of concentrated sulfuric acid to the filtrate, and evaporate to fumes. Cool, and pour the solution into a 100-ml. graduate. Add 5 ml. of quinalizarin reagent solution, dilute to 100 ml. with concentrated sulfuric acid, and mix. Place the graduate on a white marble slab or other suitable background and compare the color with a standard (described below) by the reflected light from a daylight lamp located behind the tube.

The comparison standard for use in the quinalizarin test should be prepared as follows:

Transfer 1 gram of boron-free steel to a 500-ml. flask, and add 5.7 mg. of C.P. boric acid and 15 ml. of 1:5 sulfuric acid. Heat under a reflux condenser, and proceed in the same manner as described above until the electrolyzed sample is evaporated to fumes. Cool, and dilute to 95 ml. with concentrated sulfuric acid. Each milliliter of this solution will contain 0.001 percent boron. Add 5 ml. of the quinalizarin reagent solution, and mix. Transfer to a Nessler tube, and compare the color with that of the unknown.

Special Aspects of the Quinalizarin Test. - Beryllium and magnesium interfere with this determination, as quinalizarin reacts with these elements.

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The determination can be made only in concentrated sulfuric acid; other acids produce no color with quinalizarin.

Iron, manganese, chromium, etc., do not affect the color so long as boron is present and the steel solution is in concentrated sulfuric acid.

Keeping ferric sulfate clear in solution in concentrated sulfuric acid is difficult. To obtain a clear solution in concentrated sulfuric acid, the iron and the other constituents of the steel must be removed, preferably by electrolysis.

The same volume of quinalizarin solution must be used for all determinations. A quinalizarin blank in a separate tube must be used to verify the change of colors from plain purple (color of quinalizarin in concentrated sulfuric acid) to light blue and then to deeper blue. The purple color begins to disappear at 0.008 percent boron, and the solution assumes a light blue color at 0.01 percent boron. Deeper blue colors will be observed when the sample contains more than 0.01 percent boron.

The quinalizarin test for boron in steel is simple and rapid. The color change is so sharp that the presence of 0.001 percent boron in the quinalizarin solution can be noticed easily.

H. Colorimetric Method Using Curcumin

The curcumin reagent used in this test is prepared as follows: Add 100 mg. of curcumin to 100 ml. of 95 percent ethyl alcohol in a stoppered bottle, and shake to dissolve. Allow to settle overnight, and filter. This reagent is applied to the determination of boron in steel as follows:

Transfer 2 grams of the steel to a 500-ml. flask, and add 25 ml. of 1:1 hydrochloric acid. Heat on an electric plate under a reflux condenser until the action is complete. Oxidize with one or two crystals of potassium chlorate dropped through the condenser, and boil for 15 minutes. Cool, and transfer the solution to a flat-bottom platinum dish. Add 10 percent sodium hydroxide, prepared in another platinum dish, until the solution is alkaline, and add 5 ml. in excess. Boil 1 minute, and allow to cool. Dilute to 200 ml., and mix thoroughly by pouring from one platinum dish into the other four or five times. Filter 100 ml. (equivalent to a 1-gram portion) into a platinum dish, and acidify with hydrochloric acid. Transfer the solution to a new casserole and add 0.5 gram of oxalic acid. Add 0.5 ml. of curcumin solution for each estimated 0.01 percent of boron present, and evaporate to dryness on a steam bath.

The color of the dried mass at this stage is important. A white color with a yellow cast indicates the absence of boron, while a red color indicates its presence. If too much curcumin is used, a definite orange shade appears. In this case, the portion must be discarded and the operation repeated on the remaining aliquot, using less curcumin.

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If the red color appears, cool and dissolve the salts in 100 ml. of cold distilled water. Filter, and wash with cold water. Discard the filtrate, and place a 100-ml. graduate under the funnel. Add 10 ml. of 95-percent ethyl alcohol to the residue in the casserole, agitate to dissolve, and transfer to the filter paper. Repeat this operation three or four times to wash all the colored boron compound out of the casserole and filter paper. Dilute with alcohol to 50 or 100 ml., and compare the color with a standard (described below) in a colorimeter. The comparison standard for the curcumin test is prepared as follows:

Transfer 2 grams of boron-free steel of the same general composition as the one being tested to a 500-ml. flask; add 25 ml. of 1:1 hydrochloric acid and 5.7 mg. of C. P. boric acid (equivalent to 1 mg. of boron). Heat to dissolve, and proceed as described above until the solution is evaporated to dryness. Take up with alcohol, and compare the color with the unknown in a colorimeter. If desired, a series of standard colors may be prepared by dilution, using 0.002 percent boron as gradations.

Special Aspects of Curcumin Test. - Iron, manganese, chromium, etc., must be removed by sodium hydroxide because they mask the color of red boron compounds. Sulfates must be absent, as they destroy the red color when evaporated to dryness. Chlorides do no harm, and a slightly acid HCl solution is the most favorable medium for the action of curcumin with boron in the presence of oxalic acid. Beryllium must also be absent because curcumin reacts in the same manner with it as with boron.

Selection of the dishes to be used for boron determinations is important. Practically all glass and porcelain ware contains boron. Therefore, alkaline solutions must not be placed in such dishes. Flat platinum dishes are most suitable for this kind of work. Final evaporation of slightly acid solutions can be made in new casseroles.

The use of curcumin must be controlled so that any excess will be avoided. Curcumin does not combine with sodium salts. Excess of curcumin will separate out in its original state by evaporation; both the curcumin and boron compound will dissolve in alcohol and thus will dilute the color because the color of curcumin is orange yellow in alcohol, and the color of boron is deep red in alcohol.

Piggott(22) believes that, in Kar's adaptations of the quinalizarin and curcumin tests, the conditions are somewhat critical.

Corbett and Williams(125) examined the colorimetric method developed by the Youngstown Sheet & Tube Co. for determining the percentage of boron in steel and found it simple, accurate, precise, and rapid. Rudolph and Flickinger(25) report that this method is accurate to ±0.0005 percent. A careful analyst, using the same reagents for his samples as he uses to make his standards, can readily detect 0.0002 percent boron in either the soluble or insoluble portion of the steel.

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Ordinary glassware is used. The authors of this method use bacteria culture tubes for dissolving the sample, pyrex or plain glass funnels for filtering, and 125-ml. flint-glass oil-sample bottles for comparison.

It is necessary for the analyst to have his glassware clean and dry, since any dilution of the final strength of sulfuric acid influences the depth of color. A sufficient amount of the 98.5 percent sulfuric acid and quinalizarin reagent should be made to provide a supply to last 2 or 3 months. The standard colors last almost indefinitely if kept tightly stoppered but should be remade whenever a new supply of the 98.5 percent H_2SO_4 is prepared.

An experienced analyst can determine boron in 15 to 20 samples of steel in 8 hours by this colorimetric method.

I. Colorimetric Method of the Youngstown Sheet & Tube Co.

Reagents. - Sulfuric acid (98.5 percent by weight). - To 1200 ml. of ordinary concentrated sulfuric acid (specific gravity 1.84, 95.5 percent) add 600 ml. fuming sulfuric acid (20 percent), mix well, and allow to cool. This should be kept tightly stoppered while not being used. Store in a glass-stoppered bottle.

Quinalizarin solution. - Dissolve 0.01 gram of quinalizarin (Eastman Kodak Co. 2787) in 100 ml. of strong sulfuric acid made by slowly adding 9 volumes of 98.5 percent by weight sulfuric acid to 1 volume of H_2O. Store in a glass-stoppered bottle.

Standard boric acid solutions. - Dissolve 2.8578 grams of boric acid in 1,000 ml. of distilled water. This solution contains 0.5 mg. of boron per milliliter and serves as the primary (A) base stock solution. Prepare a second (B) stock solution containing 0.01 mg. of boron per milliliter by diluting 20 ml. of (A) stock solution to 1,000 ml. with distilled H_2O and a third (C) stock solution containing 0.001 mg. of boron per milliliter by diluting 100 ml. of the second (B) stock solution to 1,000 ml.

Dilute sulfuric acid (1-4). - To 400 ml. of distilled water, slowly add 100 ml. of concentrated sulfuric acid, specific gravity 1.84. When cool, dilute to 500 ml. Store in a glass-stoppered bottle.

Apparatus. - Test tubes 17 cm. long, with inside diameter 1.8 cm., marked with a file at 10 ml.

Air condensers. - Glass tubes 3 ml. inside diameter, about 70 cm. long, each fitted on one end with a No. 3 one-hole rubber stopper to fit the test tubes.

Bottle for developing the color of standards and samples. - Preferably glass-stoppered, having at least 50-ml. capacity, with inside diameter of 3 cm. The final solution in these bottles will have a depth approximately the same as the diameter.

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After these standards are measured into dry comparison bottles, 20 ml. of the 98.5 percent H_2SO_4 are added slowly and stoppered. When cool, 1.0 ml. of the quinalizarin solution from a pipette is added and the solution mixed by gently swirling and stoppered tightly. After 15 minutes, the colors become fully developed and are ready for use. They are permanent if kept stoppered to prevent absorption of water.

One-gram portions of Bureau of Standards sample 55-a or other boron-free steel are weighed into seven dry, marked, test tubes and treated as indicated in table 5.

Procedure. - One gram of the steel to be tested is placed in a marked test tube, 8 ml. of H_2SO_4 (1-4) are added, and the test tube is stoppered with an air condenser and placed in a beaker of hot water. When all action ceases, remove the test tube, and cool with running water. Disconnect the air condenser, and wash down the inside with two 0.5-ml. portions of water, collecting these washings in the test tube. Dilute to the 10-ml. mark with distilled water, mix thoroughly, and filter through a close, dry, 9-cm. paper, collecting the filtrate in a dry, small beaker or test tube. (Reserve. This filtrate contains the boron which is soluble in H_2SO_4 (1-4).)

Replace the beaker or test tube with another, and wash the paper with distilled water, then with dilute H_2SO_4 (1-20) and finally with water to remove all acid. Discard the washings. After all washings have drained from the paper, scatter 0.5 gram of Na_2CO_3 on the inside of the paper. Place in a small platinum crucible (about 10- to 15-ml. capacity; a crucible used for volatile matter in coal will suffice), and ignite at a low temperature. When all or nearly all the paper is burned off, increase the temperature, and fuse the residue in 15 to 20 minutes. Allow to cool, and add 5 ml. of distilled water, then slowly add dropwise H_2SO_4 (1-1) until all is dissolved and the solution is slightly acid. Avoid an excess of more than 4 or 5 drops. Transfer to a marked test tube, and rinse the crucible with two 1-ml. portions of water, add approximately 0.02 gram of $Na_2S_2O_3$, cool, dilute to the 10-ml. mark, and mix well. This solution contains the boron which is insoluble in H_2SO_4 (1-4).

Pipette 2.0-ml. aliquots of each of the two foregoing prepared portions into dry comparison bottles. Slowly add 20 ml. of 98.5 percent H_2SO_4 to each, stopper, cool, and then add 1.0 ml. of the quinalizarin solution from a pipette, stopper, and mix by swirling gently. The salts formed in the bottle containing the acid-soluble portion will settle sufficiently for comparison after standing for an hour (preferably overnight) while the color produced in the acid-insoluble portion may be compared after standing 15 minutes, since no salts are precipitated.

By starting smaller samples than 1.0 gram and/or by using smaller aliquots, greater percentages of boron may be determined.

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TABLE 4. - Standards for boron in H_2SO_4 (1-4) insoluble portions of steel

No. of sample	Boron in colored standards, mg.	Distilled water, ml.	Boron B and C solutions, ml.	Boron in sample using 0.2-gram aliquot, percent
1	0.0000	2.00	0.00	Nil
2	.0010	1.00	1.00(C)	0.0005
3	.0020	.00	2.00(C)	.0010
4	.0030	1.70	.30(B)	.0015
5	.0040	1.60	.40(B)	.0020
6	.0050	1.50	.50(B)	.0025
7	.0060	1.40	.60(B)	.0030

TABLE 5. - Standards for boron in H_2SO_4 (1-4) soluble portion of steel

No. of sample	Boron in 1-gram sample, mg.	Concentrated H_2SO_4, sp.gr. 1.84, ml.	Boron B and C solution, ml.	Distilled H_2O, ml.	Boron in sample using 0.2-gram aliquot, percent
1	0.0000	1.5	0.00	6.50	Nil
2	.0050	1.5	5.00(C)	1.50	0.0005
3	.0100	1.5	1.00(B)	5.50	.0010
4	.0150	1.5	1.50(B)	5.00	.0015
5	.0200	1.5	2.00(B)	4.50	.0020
6	.0250	1.5	2.50(B)	4.00	.0025
7	.0300	1.5	3.00(B)	3.50	.0030

In general, end results as obtained by the colorimetric method are comparable in accuracy to those obtained by the distillation-titration method.

J. Colorimetric Method of Weinberg, Proctor, and Milner

Weinberg and others(27) suggested a rapid procedure for the determination of small amounts of boron, ranging from 0.001 to 0.005 percent, in corrosion-resistant steels. The sample is dissolved in dilute HCl under a reflux condenser. Hydrogen peroxide is added to decompose carbides, and the excess is decomposed by boiling. The insoluble material is filtered, fused with Na_2CO_3, and combined with the main solution. The solution is adjusted to volume, made just alkaline to litmus with sodium hydroxide pellets, and filtered. A clear aliquot portion of the filtrate is acidified with H_2SO_4 and evaporated to SO_3 fumes. Acid evaporation without loss of boric acid is possible in the presence of alkali salts. The volume is adjusted with concentrated H_2SO_4, and quinalizarin solution added. After full development of color, the solution is compared either visually or on the photoelectric colorimeter. This method is satisfactory for routine use in highly colored solutions where the boron cannot be determined directly.

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K. Woodward Method

Woodward(27) satisfactorily substituted Chromotrop 2B (p-nitrobenzene-azo-chromotropic acid) for quinalizarin in steel analysis. The reagent is less sensitive than quinalizarin to boron.

L. Electrometric Method of Campbell and Fay

Campbell and Fay(135) developed an electrometric method for determining boron in steel. The solution resulting from the precipitation and filtration of the iron is placed in a small (200-ml.) beaker. A Clark hydrogen electrode is then introduced, and as soon as the hydrogen flow has become steady, the tip of a tube leading to a standard calonel element is placed as near the hydrogen electrode as possible. This tube contains a saturated solution of potassium chloride, as does also the calomel element, and the tip is loosely plugged with cotton to minimize diffusion. There is thus formed a voltaic cell, the electromotive force of which depends solely upon the concentration of hydrogen ions in the boric solution. This e.m.f. was measured by means of a potentiometer, using a wall galvanometer of about 5,000 ohms resistance. The boric acid concentration corresponding to a given value of E may be computed from the relations:

$$E = 0.2495 + 0.0591 \log H^+,$$

$$K = \frac{H^+ (H_2BO_3)^-}{H_3BO_3},$$

where K is the equilibrium constant for the primary dissociation of the orthoboric acid and has the mean value 6.61×10^{-10} at 25° C. The term H_3BO_3 represents the equilibrium concentration of boric acid; but this may be taken as giving the total concentration with an error of less than 0.05 percent when this concentration is less than 10^{-2} equivalents per liter. The equivalents per liter of boric acid being known, the weight of boron may be computed at once from the fact that equivalent H_3BO_3 x 11 = grams of boron.

A few precautions must be observed in using this method. First, all solutions must be free of carbon dioxide. Second, since the resistance of boric solution is extremely high, being of the same order as that of good distilled H_2O, every means must be employed to minimize the effect of this resistance. The actual ohmic resistance of this part of the circuit varies directly as the length of the path; hence the tip of the tube connecting with the calomel element should be placed as close as possible to the electrode. Further, since the presence of any other ions of greater mobility than those of the boric acid has a marked effect on the e.m.f., the tube from the calomel element should not be introduced until everything is ready - that is, until a setting for null point can be obtained in the shortest possible time - otherwise, diffusion of chloride and potassium ions will throw the determination out entirely. The presence of gases other than hydrogen in the platinum electrode is especially to be guarded against.

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Atmospheric oxygen is the most common of these; it may be removed by making the electrode the cathode in an electrolysis cell, in which case the oxygen is reduced to water. When the electrode is not in use it should be kept in a stoppered jar of distilled water. With all precautions duly observed, the ultimate accuracy of setting of the potentiometer was found to be ±0.00005 volt. The resulting accuracy in boron percentage is, however, well within the limit of experimental error of the rest of the analytical work.

M. Crafts and Lamont Method

The method used by Crafts and Lamont(117) to determine boron in steel was developed by Porter, Napoleon, and Cunningham, of the Union Carbide & Carbon Research Laboratories, Inc. The procedure consists in dissolving the steel in phosphoric acid in a quartz flask equipped with a reflux condenser and subsequently separating the boron from the iron by cyclic distillation with methyl alcohol, the determination being finally completed colorimetrically in an electrophotometer.

N. Spectrographic Method

Masi(18) described a spectrographic method for determining boron in steel. The steel (carbon 0.63 percent, manganese 1.11 percent, phosphorus 0.027 percent, sulfur 0.032 percent) with a known amount of B_2O_3 added was dissolved in 1:1 HCl, and graphite electrodes were impregnated with the solution. With a spark source and a Zeiss Qu 24 quartz spectrograph, boron was determined over the range 0.03-2.01 percent; for the lowest concentrations the sensitivity was very small, but above 0.2 percent the accuracy was ± 5 percent. The pair of Fe/B lines which gave the most satisfactory results was 2533.8/2497.72. The optimum conditions were: slit width, 0.02 mm; 5 mm. rectangular diaphragm; distance between electrodes, 4 mm.; exposure, 2 minutes.

The spectrographic method of analysis makes no distinction between soluble and insoluble boron compounds, while the chemical methods separate and analyze those distinctly.

The following table indicates the authors' opinions of the accuracy of the methods and the ranges of boron content in which each method is useful. Information supplied by authorities other than the author of the method is so indicated in the column under remarks.

Method	Accuracy, percent	Range, percent	Remarks
Al....	±0.002	0.005-0.1	
Al....	± .0003	.0001-.005	Reported by Sayre(24)
G.....		.001- .03	
H.....		.001- .03	
I.....	± .0005	.0002	
I.....	± .0002		Reported by Lewis(24)
J.....	~ .001	.001- .005	
N.....	± 5 above 0.2 percent	.03-2.01	

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Since the writing of this manuscript the following three reports on the analytical determination of boron in steel have been abstracted. 8/ 9/ 10/

8/ Mukhina, Z. S., and Aleshin, A. F., Determination of Boron in Steel: Zavodskaya Lab., No. 1, vol. 11, 1945, pp. 23-30; Chem. Abs., No. 18, vol. 39, Sept. 20, 1945, pp. 4019-4020.

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